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EP-A- 0 092 647
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EP-A- 0 254 859
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CHEMICAL ABSTRACTS, vol. 94, no. 9, 2nd March 1981, page 637, column 1, abstract-no. 64642j, Columbus, Ohio, US; V.J. RAM: "Organosulfur compounds as potential pesticides"

JOURNAL OF MEDICINAL CHEMISTRY, vol. 27, 1984, pages 849-857; J. YANAGISAWA et al.: "Histamine H2 receptor antagonists. 1. Synthsis of N-cyano and N-carbamoyl amidine derivatives and their biological activities"

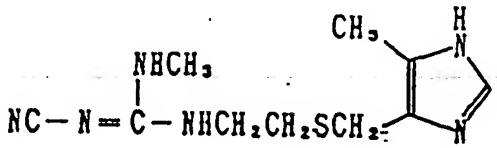
PATENT ABSTRACTS OF JAPAN, vol. 11, no. 369 (C-461)(2816), 2nd December 1987

Description

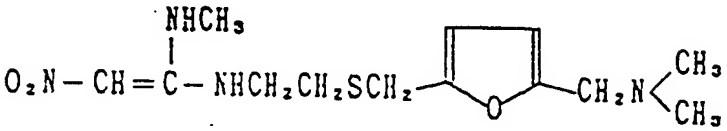
This invention relates to agrochemically useful α-unsaturated amines having insecticidal/miticidal activity, their production and use.

Among α-unsaturated amines, such compounds as (i) cimetidine (described for example in Journal of Medicinal Chemistry 24, 913, 1981),(ii) ranitidine (described for example in Agents Actions 11, 160, 1981) and (iii) famotidine (described for example in Journal of Medicinal Chemistry 27, 849, 1984)are known as histamine H_2 receptor antagonists.

(i)



(ii)



(iii)

As agricultural insecticide/miticides, organophosphorus or carbamate pesticides which are highly toxic to warm-blooded animals have heretofore been employed. However, there has been an emergence of noxious insects, particularly of the order "Hemiptera", which are resistant to these pesticides, and there has been a long-standing need for the development of a pesticide effective against these resistant pests.

EP-A-0 154 178 and EP-A-0 163 855 disclose nitromethylene-derivatives which exhibit insecticidal activity.

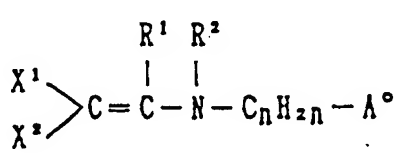
EP-A-0 302 833 which partly constitutes prior art under Art. 54(3) EPC also discloses insecticidal nitroethylene derivatives.

Getting impetus from the aforementioned histamine H_2 receptor antagonists, the present inventors synthesized various α-unsaturated amines and investigated their activities. As a result, we discovered surprisingly that compounds of the invention which have no alkylene group or only a short alkylene group in the side chain have agriculturally useful insecticidal/miticidal activity.

Based on the above finding, the present inventors conducted further research and have come up with the present invention.

The invention is, thus, concerned with:

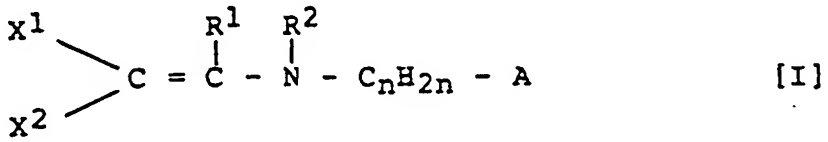
(1) novel α-unsaturated amines of the formula:



[I°]

wherein the symbols have the meaning as defined in the claims of the present invention,

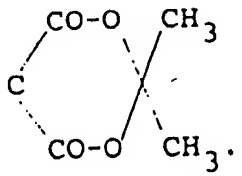
(2) insecticidal/pesticidal compositions containing an α-unsaturated amine of the formula :



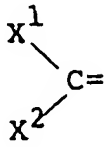
[I]

wherein the symbols have the meaning as defined in the claims of the present invention, and their production.

Referring to the above formulas [I°] and [I], one of X^1 and X^2 is an electron-attracting group with the other being a hydrogen atom or an electron-attracting group. The electron-attracting group represents by X^1 and X^2 includes, among others, cyano, nitro, C_{1-4}alkoxy-carbonyl (e.g. methoxycarbonyl, ethoxycarbonyl, etc.), hydroxycarbonyl, C_{6-10}aryloxy-carbonyl (e.g. phenoxycarbonyl etc.), heterocycleoxycarbonyl wherein the heterocycle moiety is as mentioned below (e.g. pyridyloxycarbonyl, thienyloxycarbonyl, etc.), C_{1-4}alkylsulfonyl which may be substituted with halogen (e.g. methylsulfonyl, trifluoromethylsulfonyl, ethylsulfonyl, etc.), aminosulfonyl, di-C_{1-4}alkoxyphosphoryl (e.g. diethoxyphosphoryl,etc.), C_{1-4}acyl which may be substituted with halogen (e.g. a C_{1-4}alkylcarbonyl such as acetyl, trichloroacetyl, trifluoroacetyl, etc.), C_{1-4}alkylsulfonylthiocarbamoyl (e.g. methylsulfonylthiocarbamoyl, etc.), carbamoyl and so on. One of X^1 and X^2 may be a halogen atom such as fluorine, chlorine, bromine or iodine, and X^1 and X^2 may join together with the adjacent carbon atom to form
a ring such as, for example,

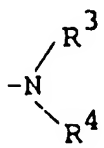


Preferred examples of the group



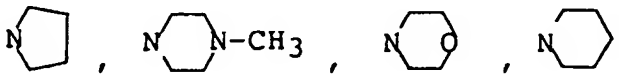
are $O_2NCH=$.

Referring to the above formulas [I°] and [I], R^1 may be a group attached through a carbon, oxygen or sulfur atom, but a group attached through a nitrogen atom is preferred. Thus, for example, a group of the formula



can be used. In the above formula, R^3 is for example a hydrogen atom, an alkyl group (for example, a C_{1-6} alkyl group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, n-hexyl, etc.), an C_{6-10}aryl group (for example, phenyl, etc.), an C_{7-9} aralkyl group (for example a phenylalkyl such as benzyl, etc.), a heterocyclic group as mentioned below (for example, pyridyl, etc.), a C_{1-4}acyl group (for example, formyl, acetyl, propionyl, etc.), a C_{6-10} arylcarbonyl (for example, benzoyl, etc.), an alkoxycarbonyl group (for

example, C_{1-4} alkoxycarbonyl groups such as methoxycarbonyl, ethoxycarbonyl, etc.), a C_{6-10} aryloxycarbonyl group (for example, phenoxycarbonyl, etc.), a heterocycleoxycarbonyl group wherein the heterocycle moiety is as mentioned below (for example, furyloxycarbonyl, etc.), a C_{6-10} arylsulfonyl group (for example, phenylsulfonyl, etc.), an alkylsulfonyl group (for example, C_{1-4} alkylsulfonyl groups such as methylsulfonyl, etc.), a dialkoxyphosphoryl group (for example, di-C_{1-4} alkoxyphosphoryl groups such as diethoxyphosphoryl, etc.), an alkoxy group (for example, C_{1-4} alkoxy groups such as methoxy, ethoxy, etc.), a hydroxy group, an amino group, a dialkylamino group (for example, di-C_{1-4} alkylamino group such as dimethylamino, diethylamino, etc.), an acylamino group (for example, C_{1-4} acylamino groups such as formylamino, acetylamino, propionylamino, etc.), an alkoxycarbonylamino groups (for example, C_{1-4} alkoxycarbonylamino groups such as methoxycarbonylamino, etc.), an alkylsulfonylamino group (for example, C_{1-4} alkylsulfonylamino groups such as methylsulfonylamino, etc.), a di-alkoxyphosphorylamino group (for example, di-C_{1-4} alkoxyphosphorylamino groups such as diethoxyphosphorylamino, etc.), an C_{7-9} aralkyloxy group (for example, benzyloxy, etc.), an alkoxycarbonylalkyl group (for example, C_{1-4} alkoxycarbonyl-C_{1-4} alkyl groups such as methoxycarbonylmethyl, etc.) or the like. R^4 is for example a hydrogen atom, or an alkyl (for example, C_{1-4} alkyl groups such as methyl, ethyl, etc.), cycloalkyl (for example, C_{3-6} cycloalkyl groups such as cyclohexyl, etc.), alkenyl (for example, C_{2-4} alkenyl groups such as vinyl, allyl, etc.), cycloalkenyl (e.g. C_{3-6} cycloalkenyl groups such as cyclohexenyl, etc.) or alkynyl (for example, C_{2-4} alkynyl groups such as ethynyl, etc.) group which may optionally be substituted by 1 to 3 substituents (e.g. hydroxyl,C_{1-4} alkoxy such as methoxy, halogen such as fluorine, di-C_{1-4} alkylamino such as dimethylamino, C_{1-4} alkylthio such as i-propylthio and n-propylthio, C_{1-3} acylamino such as acetylamino, C_{1-4} alkylsulfonylamino such as methylsulfonylamino, tri-C_{1-4} alkylsilyl such as trimethylsilyl, pyridyl or thiazolyl which may optionally be substituted with a halogen atom, etc.). Furthermore, R^3 and R^4 may, taken together with the adjacent nitrogen atom, constitute a 5- or 6-membered cyclic amino group such as



and so on.

The group attached through a nitrogen atom, represented by R^1, includes an amino group which may optionally be substituted (for example by any of the alkyl, aryl, aralkyl, heterocyclic, acyl, alkoxycarbonyl, aryloxycarbonyl, heterocycleoxycarbonyl, arylsulfonyl, alkylsulfonyl, dialkoxyphosphoryl, cycloalkyl, alkenyl, cycloalkenyl and alkynyl groups mentioned in the above definition of R^3 and R^4) such as di-substituted amino groups, e.g. di-C_{1-6} alkylamino, N-C_{1-6} alkyl-N-formylamino, etc., mono-substituted amino groups, e.g. mono-C_{1-6} alkylamino etc., and unsubstituted amino, a hydrazino group which may optionally be substituted (for example by any of the alkyl, acyl, alkoxycarbonyl, alkylsulfonyl, dialkoxyphosphoryl and other groups mentioned in the above definition of R^3) or a hydroxyamino group which may optionally be substituted (for example by any of the alkyl, aralkyl and other groups mentioned in the above description of R^3).

R^2 is a hydrogen atom or a group attached through a carbon, nitrogen or oxygen atom. The group attached through a carbon atom, R^2, includes, among others, C_{1-4} acyl (for example, formyl, acetyl, propionyl, etc.), alkyl (for example, C_{1-4} alkyl groups such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, etc.), alkenyl (for example, C_{2-4} alkenyl groups such as vinyl, allyl, etc.), cycloalkyl (for example, C_{3-6} cycloalkyl groups such as cyclopentyl, cyclohexyl, etc.), C_{6-10} aryl (for example, phenyl, naphthyl, etc.), C_{7-9} aralkyl (for example phenylalkyl such as benzyl, etc.) and heterocyclic as mentioned below which has a free bond on a carbon atom thereof (for example, 3- or 4-pyridyl, etc.). These groups may each be substituted by 1 to 3 substituents (for example, C_{1-4} alkylthio groups such as methylthio, ethylthio, etc., C_{1-4} alkoxy groups such as methoxy, ethoxy, etc., mono- or di-C_{1-4} alkylamino groups such as methylamino, dimethylamino, etc., C_{1-4} alkoxy-carbonyl groups such as methoxycarbonyl, ethoxycarbonyl, etc., C_{1-4} alkylsulfonyl groups such as methylsulfonyl, ethylsulfonyl, etc., halogen atoms such as fluorine,chlorine, bromine iodine, etc., C_{1-4} acyl groups including alkanoyls such as acetyl, etc., benzoyl, phenylsulfonyl, pyridyl and so on). The group attached through a nitrogen atom, R^2, includes, among others, the groups mentioned in the definition of R^1. The group attached through an oxygen atom, R^2, includes, among others, alkoxy (for example, C_{1-4} alkoxy groups such as methoxy, ethoxy, etc.), cycloalkoxy (for example, C_{3-6} cycloalkoxy groups such as cyclohexyloxy etc.), alkenyloxy (for example, C_{2-4} alkenyloxy groups such as vinyloxy, allyloxy, etc.), cycloalkenyloxy (for example, C_{3-6} cycloalkenyloxy groups such as cyclohexenyloxy etc.), alkynyloxy (for example, ethynyloxy etc.), C_{6-10} aryloxy (for example, phenoxy,

etc.), heterocycleoxy wherein the heterocycle moiety is as mentioned below (for example, thienyloxy etc.) and hydroxyl. These groups may each have 1 to 3 substituents (for example, halogen such as fluorine, chlorine, bromine, phenyl and so on). R^2 is preferably a group attached through a carbon, nitrogen or oxygen group, such as formyl, an alkyl group (particularly C_{1-4} alkyl groups such as methyl, ethyl, etc.) which may optionally be substituted (for example by the C_{1-4} alkylthio, C_{1-4} alkoxy, mono- or di-C_{1-4} alkylamino, C_{1-4} alkoxycarbonyl, C_{1-4} alkylsulfonyl, acetyl, benzoyl, phenylsulfonyl, pyridyl, etc.), an amino group which may optionally be substituted (for example, those mentioned in the definition of R^1) and a hydroxyl group which may optionally be substituted, for example by the above-mentioned C_{1-4} alkyl, C_{3-6} cycloalkyl, C_{2-4} alkenyl, C_{3-6} cycloalkenyl, C_{2-4} alkynyl, C_{6-10} aryl and heterocyclic groups (particularly C_{1-4} alkoxy groups such as methoxy and so on). The symbol n means 0, 1 or 2. Therefore, $-C_nH_{2n}-$ in the formulas [I•] and [I] represents a single bond, $-CH_2-$, $-CH_2CH_2-$, or

although the single bond or $-CH_2-$ is preferred. The symbols A• and A mean a heterocyclic group as mentioned below (such as 3-pyridyl, 6-chloro-3-pyridyl, 6-methoxy-3-pyridyl, 6-methyl-3-pyridyl, 3-quinolyl, etc.), preferably one which may optionally be substituted with one to three of the choices (i), (iv), (Viii), (XVii), (XLVi), (XLViii) and so on as mentioned below, or a cyclic hydrocarbon group as mentioned below (such as cyclopropyl, cyclohexyl, phenyl, p-chlorophenyl and so on), preferably one which may optionally be substituted with one or two of the choice (XVii) as mentioned below. The heterocyclic group of A• or A is more preferably a pyridyl or thiazolyl group which may optionally be substituted, such as 3-pyridyl, 6-chloro-3-pyridyl, 6-bromo-3-pyridyl, 2-chloro-5-thiazolyl and so on. The cyclic hydrocarbon group A is more preferably a halophenyl group such as p-chlorophenyl and so on.

As the alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, aralkyl, heterocyclic and cyclic hydrocarbon groups in the definitions of X^1, X^2, R^1, R^2, R^3, R^4, A• and A, the following groups, among others, may be employed and each of these groups may have 1 to 5 substituents such as (i) through (Lii) which appear hereinafter.

The alkyl group preferably contains 1 to 20 carbon atoms and is more preferably a group of 1 to 8 carbon atoms. This alkyl group may be straight-chain or branched. Specific examples of the alkyl group include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, 2-ethylhexyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl, nonadecyl, eicosyl and so on.

The cycloalkyl group is preferably a group of 3 to 6 carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and so on.

The alkenyl group is preferably a group of 2 to 6 carbon atoms. Specific examples of such alkenyl group include vinyl, allyl, isopropenyl, methallyl, 1,1-dimethylallyl, 2-butenyl, 3-butenyl, 2-pentenyl, 4-pentenyl, 5-hexenyl and so on.

The cycloalkenyl group is preferably a group of 3 to 6 carbon atoms, such as 1-cyclopropenyl, 2-cyclopropenyl, 1-cyclobutenyl, 2-cyclobutenyl, 1-cyclopentenyl, 2-cyclopentenyl, 3-cyclopentenyl, 1-cyclohexenyl, 2-cyclohexenyl, 3-cyclohexenyl, 1,3-cyclohexadien-1-yl, 1,4-cyclohexadien-1-yl, 1,3-cyclopentadien-1-yl,2,4-cyclopentadien-1-yl and so on.

The alkynyl group is preferably a group of 2 to 6 carbon atoms, such as ethynyl, propargyl, 2-butyn-1-yl, 3-butyn-1-yl, 3-butyn-2-yl, 1-pentyn-3-yl, 3-pentyn-1-yl, 4-pentyn-2-yl, 3-hexyn-1-yl and so on.

The aryl group may for example be phenyl or naphthyl.

The aralkyl group may for example be benzyl, phenethyl, naphthylmethyl or the like.

The heterocyclic group includes, among others, 5- to 8-membered rings each containing 1 to 5 hetero atoms such as oxygen, sulfur and nitrogen or fused rings derived therefrom, such as 2- or 3- thienyl, 2- or 3- furyl, 2- or 3- pyrrolyl, 2-, 3- or 4- pyridyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5- thiazolyl, 3-, 4- or 5- pyrazolyl, 2-, 4- or 5- imidazolyl, 3-, 4- or 5- isoxazolyl, 3-, 4- or 5- isothiazolyl, 3- or 5- (1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H tetrazolyl, N-oxido- 2-, 3- or 4- pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxido-2-, 4- or 5- pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxido-3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, in-

dolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, phenoxazinyl and so on.

The cyclic hydrocarbon group includes, among others, C_{3-6} cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, etc., C_{3-6} cycloalkenyl groups such as 1-cyclopropenyl, 2-cyclobutenyl, 1-cyclohexenyl, 2-cyclohexenyl, 1,3-cyclohexadien-1-yl, etc., and C_{6-10} aryl groups such as phenyl, naphthyl and so on.

(i) C_{1-4} Alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, etc. are used.

(ii) C_{3-6} Cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, etc. are used.

(iii) C_{6-10} Aryl groups such as phenyl, naphthyl, etc. are used.

(iv) C_{1-4} Alkoxy groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, etc. are used.

(v) C_{3-6} Cycloalkyloxy groups such as cyclopropyloxy, cyclopentyloxy, cyclohexyloxy, etc. are used.

(vi) C_{6-10} Aryloxy groups such as phenoxy, naphthyloxy, etc. are used.

(vii) C_{7-12} Aralkyloxy groups such as benzyloxy, 2-phenethyloxy, 1-phenethyloxy, etc. are used.

(viii)C_{1-4} Alkylthio groups such as methylthio, ethylthio, propylthio, butylthio, etc. are used.

(ix) C_{3-6} Cycloalkylthio groups such as cyclopropylthio, cyclopentylthio, cyclohexylthio, etc. are used.

(x) C_{6-10} Arylthio groups such as phenylthio, naphthylthio, etc. are used.

(xi) C_{7-12} Aralkylthio groups such as benzylthio, 2-phenethylthio, 1-phenethylthio, etc. are used.

(xii) Mono-C_{1-4} alkylamino groups such as methylamino, ethylamino, propylamino, isopropylamino, butylamino, isobutylamino, tert-butylamino, etc. are used.

(xiii)Di-C_{1-4} alkylamino groups such as dimethylamino, diethylamino, dipropylamino, dibutylamino, N-methyl-N-ethylamino, N-methyl-N-propylamino, N-methyl-N-butylamino, etc. are used.

(xiv) C_{3-6} Cycloalkylamino groups such as cyclopropylamino, cyclopentylamino, cyclohexylamino, etc. are used.

(xv) C_{6-10} Arylamino groups such as anilino etc. are used.

(xvi) C_{7-12} Aralkylamino groups such as benzylamino, 2-phenethylamino, 1-phenethylamino, etc. are used.

(xvii)Halogen atoms such as fluorine, chlorine, bromine and iodine are used.

(xviii)C_{1-4} Alkoxycarbonyl groups such as methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarboyl, butoxycarbonyl, tert-butoxycarbonyl, isobutoxycarbonyl, etc. are used.

(xix) C_{6-10} Aryloxycarbonyl groups such as phenoxycarbonyl etc. are used.

(xx) C_{3-6} Cycloalkyloxycarbonyl groups such as cyclopropyloxycarbonyl, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, etc. are used.

(xxi) C_{7-12} Aralkyloxycarbonyl groups such as benzyloxycarbonyl, 1-phenethyloxycarbonyl, 2-phenethyloxycarbonyl, etc. are used.

(xxii)C_{1-5} Alkanoyl groups such as formyl, acetyl, propionyl, butyryl, pivaloyl, etc. are used.

(xxiii)C_{1-15} Alkanoyloxy groups such as formyloxy, acetoxy, butyryloxy, pivaloyloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, etc. are used.

(xxiv)Carbamoyl groups which may optionally be substituted, such as carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-ethylcarbamoyl, N,N-diethylcarbamoyl, N-phenylcarbamoyl, pyrrolidinocarbamoyl, piperidinocarbamoyl, piperazinocarbamoyl, morpholinocarbamoyl, N-benzylcarbamoyl, etc. are used.

(xxv) Substituted carbamoyloxy groups such as N-methylcarbamoyloxy, N,N-dimethylcarbamoyloxy, N-ethylcarbamoyloxy, N-benzylcarbamoyloxy, N,N-dibenzylcarbamoyloxy, N-phenylcarbamoyloxy, etc. are used.

(xxvi)C_{1-4} Alkanoylamino groups such as formylamino, acetamido, propionamide, butyramido, etc. are used.

(xxvii)C_{6-10} Arylcarbonylamino groups such as benzamido etc. are used.

(xxviii)C_{1-4} Alkoxycarbonylamino groups such as methoxycarbonylamino, ethoxycarbonylamino, butoxycarbonylamino, tert-butoxycarbonylamino, etc. are used.

(xxix)C_{7-12} Aralkyloxycarbonylamino groups such as benzyloxycarbonylamino, 4-methoxybenzyloxycarbonylamino, 4-nitrobenzyloxycarbonylamino, 4-chlorobenzyloxycarbonylamino, etc. are used.

(xxx) Substituted sulfonylamino groups such as methanesulfonylamino, ethanesulfonylamino, butanesulfonylamino, benzensulfonylamino, toluenesulfonylamino, naphthalenesulfonylamino, trifluoromethanesulfonylamino, 2-chloroethanesulfonylamino, 2,2,2-trifluoromethanesulfonylamino, etc. are used.

(xxxi)Heterocyclic groups nuclearly containing 1 to 5 hetero atoms of N, O and/or S, such as pyrrolidinyl, pyrrolyl, pyrazolyl, imidazolyl, furyl, thienyl, oxazolyl, isoxazolyl, isothiazolyl, thiazolyl, piperidinyl, pyridyl, piperazinyl, pyrimidinyl, pyranyl, tetrahydropyranyl, tetrahydrofuryl, indolyl, quinolyl, 1,3,4-oxadiazolyl, thieno[2,3-d]pyridyl, 1,2,3-thiadiazolyl, 1,3,4-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1,3,4-triazolyl, tetrazolyl, 4,5-dihydro-1,3-dioxazolyl, tetrazolo[1,5-b]pyridazinyl, benzothiazolyl, benzoxazolyl, benzimidazolyl, benzothienyl, etc. are used.

(xxxii)Heterocyclethio, heterocycleoxy, heterocycleamino, and heterocyclecarbonylamino groups and groups derived therefrom by attachment of any of heterocyclic groups (xxxi) to the S, O, N atom or the carbonylamino group are used.

(xxxiii)Di-C_{1-4} alkylphosphinothioylamino groups such as dimethylphosphinothioylamino, diethylphosphinothioylamino, etc. are used.

(xxxiv)Alkoxyimino groups such as methoxyimino, ethoxyimino, 2-fluoroethoxyimino, carboxymethoxyimino, 1-carboxy-1-methylethoxyimino, 2,2,2-trichloroethoxycarbonylmethoxyimino, 1-(2,2,2-trichloroethoxycarbonyl)-1-methylethoxyimino, (2-aminothiazol-4-yl)methoxyimino, (1H-imidazol-4-yl)-methoxyimino, etc. are used.

(xxxv)C_{1-4} Alkylsulfonyloxy groups such as methanesulfonyloxy, ethanesulfonyloxy, butanesulfonyloxy, etc. are used.

(xxxvi)C_{6-10} Arylsulfonyloxy groups such as benzenesulfonyloxy, toluenesulfonyloxy, etc. are used.

(xxxvii) Di-C_{6-10} arylphosphinothioylamino groups such as diphenylphosphinothioylamino, etc. are used.

(xxxviii)Thiocarbamoylthio groups which may optionally be substituted, such as thiocarbamoylthio, N-methylthiocarbamoylthio, N,N-dimethylthiocarbamoylthio, N-ethylthiocarbamoylthio, N-benzylthiocarbamoylthio, N,N-dibenzylthiocarbamoylthio, N-phenylthiocarbamoylthio, etc. are used.

(xxxix)Silyloxy groups such as trimethylsilyloxy, t-butyldimethylsilyloxy, t-butyldiphenylsilyloxy, dimethylphenylsilyloxy, etc. are used.

(xL) Silyl groups such as trimethylsilyl, t-butyldimethylsilyl, t-butyldiphenylsilyl, dimethylphenylsilyl, etc. are used.

(xLi) C_{1-4} Alkylsulfinyl groups such as methylsulfinyl, ethylsulfinyl, propylsulfinyl, butylsulfinyl, etc. are used.

(xLii)C_{6-10} Arylsulfinyl groups such as phenylsulfinyl, naphthylsulfinyl, etc. are used.

(xLiii)C_{1-4} Alkylsulfonyl groups such as methanesulfonyl, ethanesulfonyl, butanesulfonyl, etc. are used.

(xLiv)C_{6-10} Arylsulfonyl groups such as benzenesulfonyl, toluenesulfonyl, etc. are used.

(xLv) C_{1-4} Alkoxycarbonyloxy groups such as methoxycarbonyloxy, ethoxycarbonyloxy, tert-butoxycarbonyloxy, etc. are used.

(xLvi)Halo-C_{1-4} alkyl groups such as trifluoromethyl, 1,1,2,2-tetrafluoroethyl, difluoromethyl, monofluoromethyl, trichloromethyl, dichloromethyl, monochloromethyl, etc. are used.

(xLvii)Halo-C_{1-4} alkoxy, halo-C_{1-4} alkylthio, halo-C_{1-4} alkylsulfinyl and halo-C_{1-4} alkylsulfonyl groups as well as groups derived therefrom by attachement of any of halo-C_{1-4} alkyl groups (xLvi) to the O, S, sulfinyl and sulfonyl moieties thereof are used.

(xLviii)Cyano, nitro, hydroxy, carboxyl, sulfo and phosphono groups are used.

(xLix)C_{1-4} Alkyloxysulfonyl groups such as methoxysulfonyl, ethoxysulfonyl, butoxysulfonyl, etc. are used.

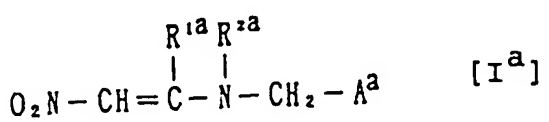
(L) C_{6-10} Aryloxysulfonyl groups such as phenoxysulfonyl, tolyloxysulfonyl, etc. are used.

(Li) C_{7-12} Aralkyloxysulfonyl groups such as benzyloxysulfonyl, 2-phenethyloxysulfonyl, 1-phenethyloxysulfonyl, etc. are used.

(Lii) Di-C_{1-4}-alkyloxyphosphoryl groups such as dimethoxyphosphoryl, diethoxyphosphoryl, dibutoxyphosphoryl, etc. are used.

Preferred examples of the unsaturated amines of formulas [I•] and [I] or salts thereof include:

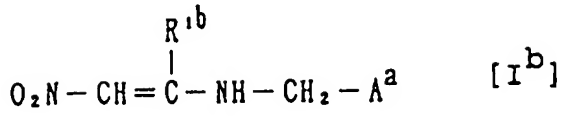
The α-unsaturated amines of the formula:



[I^a]

wherein R^{1a} is a mono-C_{1-6} alkylamino group, an N-C_{1-6} alkyl-N-formylamino group or an amino group; $R^{2a}$is an C_{1-4} alkyl group or an C_{1-4} alkoxy group; A^a is a chloropyridyl group, or salts thereof;

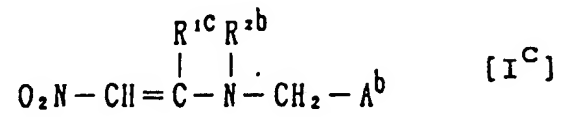
the α-unsaturated amines of the formula:



[I^b]

wherein R^{1b} is a mono-C_{1-6} alkylamino group or an N-C_{1-6} alkyl-N-formylamino group; A^a has the meaning defined hereinbefore, or salts thereof;

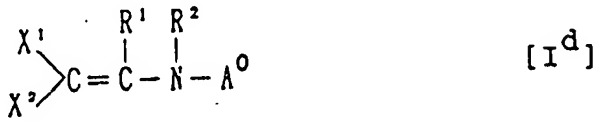
the α-unsaturated amines of the formula:



[I^c]

wherein R^{1c} is a di-C_{1-6} alkylamino group; R^{2b} is a hydrogen atom, a formyl group or an C_{1-4} alkyl group; A^b is a pyridyl group or a chloropyridyl group, or salts thereof; and

the α-unsaturated amines of the formula:



[I^d]

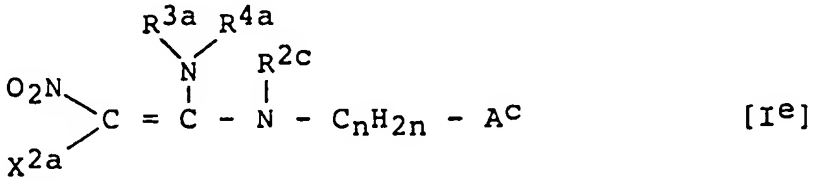
wherein the symbols have the meanings defined hereinbefore, or salts thereof.

Referring to the above formulas [I^a], [I^b] and [I^c], the mono-C_{1-6} alkylamino group represented by R^{1a} or R^{1b} includes, among others, monomethylamino, monoethylamino, mono-n-propylamino, mono-i-propylamino, mono-n-butylamino, mono-i-butylamino, mono-n-hexylamino, etc. and preferably mono-C_{1-4}-alkyl amino groups such as mono-methylamino, monoethylamino and so on. The N-C_{1-6} alkyl-N-formylamino group represented by R^{1a} or R^{1b} includes, among others, N-methyl-N-formylamino, N-ethyl-N-formylamino, N-n-propyl-N-formylamino, N-i-propyl-N-formylamino, N-n-butyl-N-formylamino, N-n-hexyl-N-formylamino, etc. and preferably N-C_{1-4} alkyl-N-formylamino groups such as N-methyl-N-formylamino, N-ethyl-N-formylamino and so on. The di-C_{1-6} alkylamino group represented by R^{1c} includes, among others, dimethylamino, N-ethyl-N-methylamino, diethylamino, di-n-propylamino, di-i-propylamino, di-n-butylamino, di-i-butylamino, di-n-pentylamino, di-i-pentylamino, di-n-hexylamino, etc. and preferably di-C_{1-4} alkylamino groups such as dimethylamino, N-ethyl-N-methylamino and diethylamino.

The C_{1-4} alkyl group represented by R^{2a} or R^{2c} includes, among others, the alkyl groups mentioned in the definition of R^2 above and preferably methyl, ethyl and so on. The C_{1-4} alkoxy group represented by R^{2a} includes, among others, the alkoxy groups mentioned in the definition of R^2 above and preferably methoxy, ethoxy and so on. The chloropyridyl group represented by A^a or A^b includes, among others, 2-chloro-3-pyridyl, 4-chloro-3-pyridyl, 5-chloro-3-pyridyl, 6-chloro-3-pyridyl, 3-chloro-4-pyridyl, etc. and preferably 6-chloro-3-pyridyl and so on. The pyridyl group represented by A^b includes 3-pyridyl, 4-pyridyl, etc. and preferably 3-pyridyl.

Typical α-unsaturated amines of formulas [I^*] and [I] or salts thereof include :

The α-unsaturated amines of the formula :

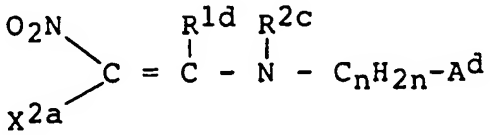


[I^e]

wherein X^{2a} is a hydrogen atom, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl; R^{2c} is a hydrogen atom, C_{1-3} acyl, C_{1-4} alkyl, mono- or di- C_{1-4} alkoxy-C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di- C_{1-4}

alkylamino or C_{1-4} alkoxy; A^c is 3- or 4- pyridyl, pyrazinyl or 4- or 5- thiazolyl which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy; and R^{3a}, R^{4a} and n are as defined above, or salts thereof;

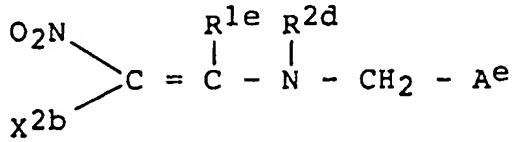
the α-unsaturated amines of the formula :



[If]

wherein X^{2a} is a hydrogen atom, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl; R^{1d} is amino, mono- or di- C_{1-4} alkylamino, N- C_{1-4} alkyl - N- C_{1-3} acylamino, C_{7-9} aralkylamino, halogenothiazolyl-C_{1-2} alkylamino or C_{1-4} alkoxy -C_{1-2} alkylamino;
R^{2c} is a hydrogen atom, C_{1-3} acyl, C_{1-4} alkyl, mono- or di- C_{1-4} alkoxy- C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di-C_{1-4} alkylamino or C_{1-4} alkoxy;
n is an integer equal to 0, 1 or 2; and A^d is 3- or 4-pyridyl, pyrazinyl or 5-thiazolyl which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy, or salts thereof;

the α-unsaturated amines of the formula :

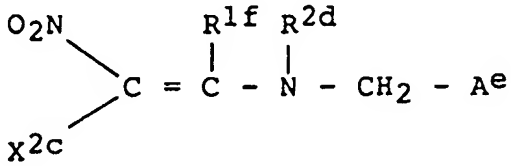


[Ig]

wherein X^{2b} is a hydrogen atom or C_{1-2}alkylsulfonylthiocarbamoyl; R^{1e} is amino, mono- or di-C_{1-2}alkylamino or N-C_{1-2}alkyl-N-formylamino; R^{2d} is a hydrogen atom, C_{1-2}alkyl or C_{1-3}acyl; and A^e is a group of the formula :

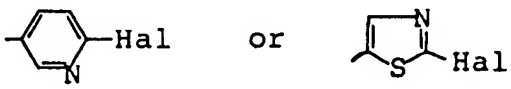
wherein Hal is a halogen atom, or salts thereof;

the α-unsaturated amines of the formula :



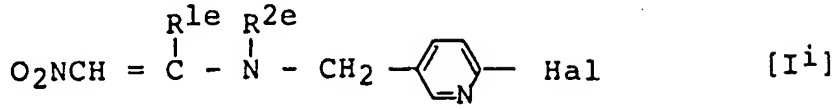
[Ih]

wherein X^{2c} is a hydrogen atom or methylsulfonylthiocarbamoyl; R^{1f} is amino, methylamino, dimethylamino or N-methyl-N-formylamino ; R^{2d} is a hydrogen atom, formyl or C_{1-2}alkyl ; and A^e is a group of the formula :



wherein Hal is a halogen atom, or salts thereof ; and

the α-unsaturated amines of the formula :



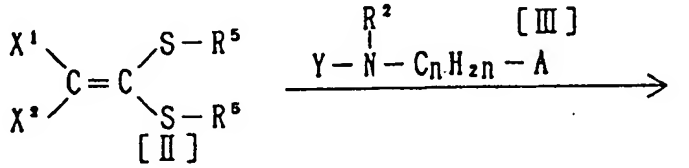
[Ii]

wherein R^{1e} is amino, mono- or di-C_{1-2}alkylamino or N-C_{1-2}alkyl-N-formylamino ; R^{2e} is C_{1-2}alkyl or formyl; and Hal is a halogen atom, or salts thereof.

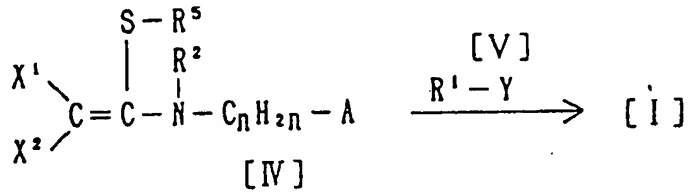
In the above formulas [Ie] to [Ii],
the groups represented by X^{2a}, X^{2b} and X^{2c},
the groups represented by R^{1d}, R^{1e} and R^{1f},
the groups represented by R^{2c}, R^{2d} and R^{2e},and
the groups represented by A^c, A^d and A^e are
as mentioned above in the case of X^2, R^1, R^2, A° and A.

The compound [I] or its salt can be produced by the analogous known processes and further by the following processes, for instance.

Process 1)

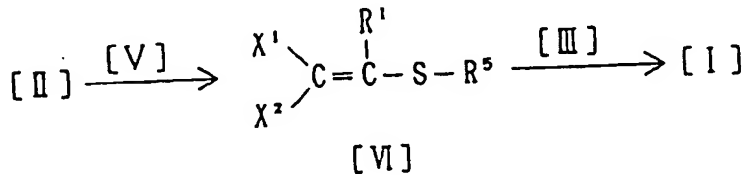


[II] [III]



[IV] [V] [I]

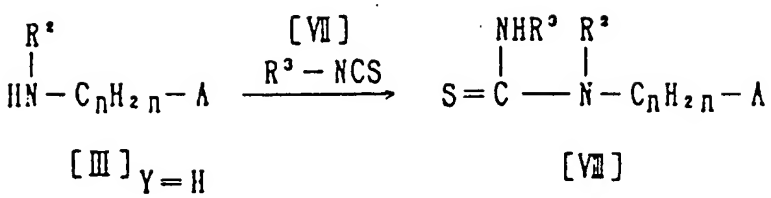
or



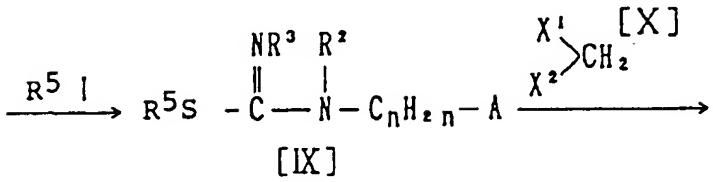
[II] [V] [VI] [III] [I]

wherein X^1, X^2, R^1, R^2, n and A have the meanings defined hereinbefore; R^5 is an C_{1-4} alkyl group such as methyl, ethyl, etc. or an C_{7-9}aralkyl group such as benzyl etc.; Y is a hydrogen atom or an alkali metal such as sodium, potassium, etc.

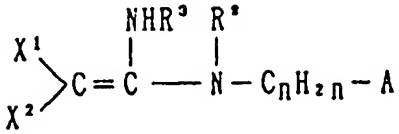
Process 2)



[III]$_{Y=H}$ [VII]

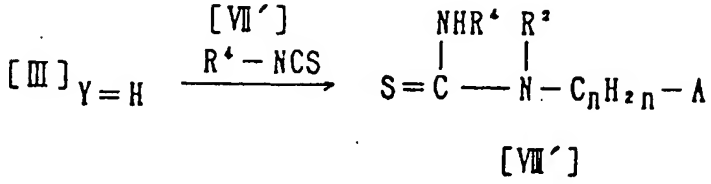


[IX] [X]

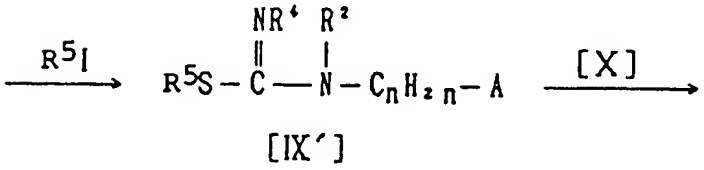


[I-1]

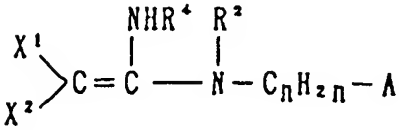
or



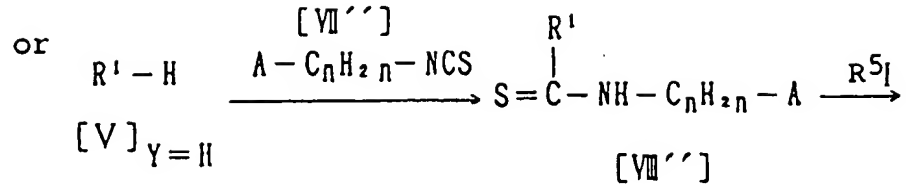
[III]$_{Y=H}$ [VII′]

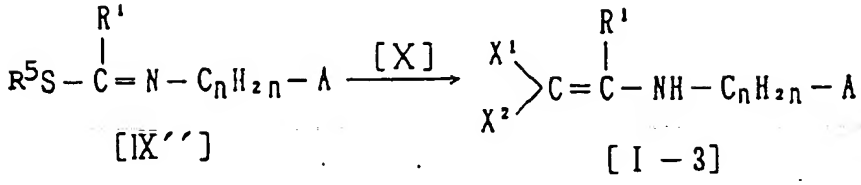


[IX′] [X]



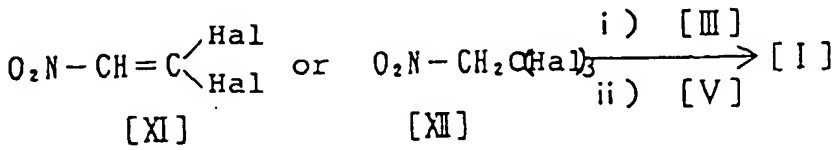
[I-2]

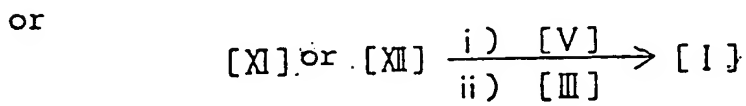




wherein X^1, X^2, R^1, R^2, R^3, R^4, R^5, n and A have the meanings defined hereinbefore.

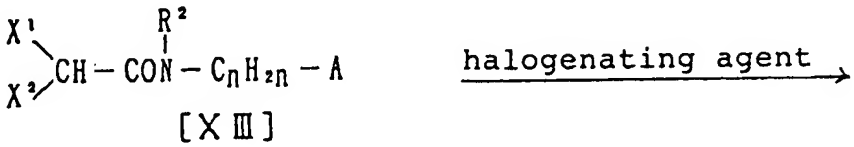
Process 3)

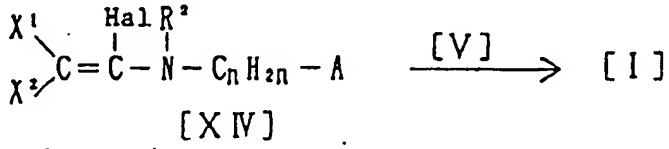


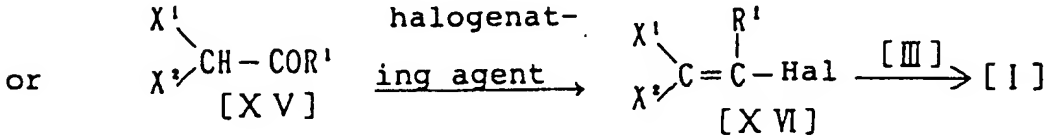


wherein Hal is the meanings defined hereinbefore.

Process 4)

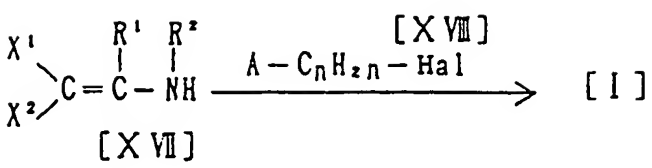






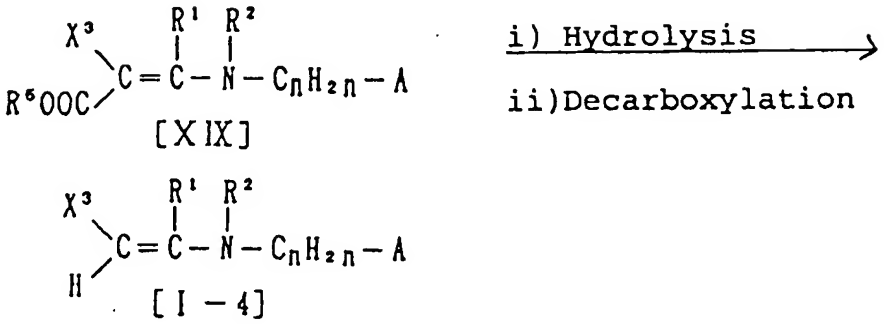
wherein X^1, X^2, R^1, R^2, Hal, n and A have the meanings defined hereinbefore.

Process 5)



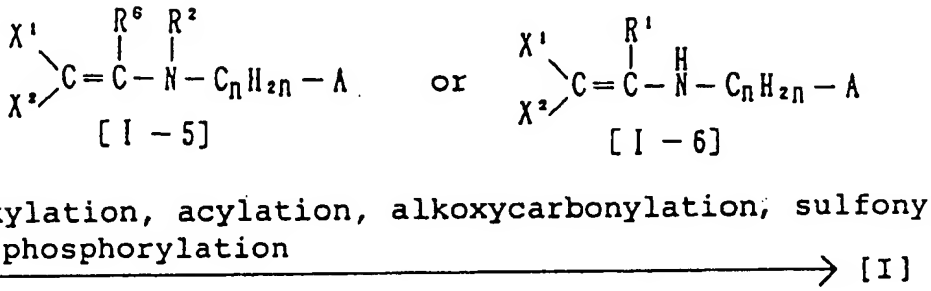
wherein X^1, X^2, R^1, R^2, Hal, n and A have the meanings defined hereinbefore.

Process 6)



wherein R^1, R^2, n, A and R^5 have the meanings defined hereinbefore; X^3 is an electron-attracting group.

Process 7)



wherein X^1, X^2, R^1, R^2, n and A have the meanings defined hereinbefore; R^5 is a group attached through a nitrogen atom containing at least one hydrogen atom.

In the processes 1) to 7), the compounds [III], [IV] [V], [VI], [XI], [IX'], [IX"], [X], [XIV], [XVI], [XVII], [XVIII], [XIX], [I-5], [I-6] and so on may be used in a form of a salt (e.g. one as mentioned below in a salt of the compound [I]).

In accordance with the aforementioned Process 1), a compound of general formula [II] is reacted with an amino compound of general formula [III] or a salt thereof to give a compound of general formula [IV] which is then reacted with an amino compound of general formula [V] or a salt thereof, or a compound of general formula [II] is reacted with a compound of general formula [V] to give a compound of general formula [VI] which is then reacted with a compound of general formula [III], to thereby give a compound [I]. In practicing the Process 1), the reactions of [II]→[IV], [IV]→[I], [II]→[VI] and [VI]→[I] may respectively be conducted in an appropriate solvent. There is no limitation on such a solvent provided that it does not

interact with the reactant, reagent or reaction product to give byproducts but a solvent capable of dissolving both the reactant and reagent is preferred. As examples of such solvent, there may be mentioned alcohols such as methanol, ethanol, propanol, butanol, etc., aromatic hydrocarbons such as benzene, toluene, xylene, etc., ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, dioxane, etc., nitriles such as acetonitrile, propionitrile, etc., acid amides such as dimethylformamide, dimethylacetamide, etc., sulfoxides such as dimethyl fulfoxide,etc., sulfones such as sulfolane, etc., and phosphoramides such as hexamethylphosphoramide etc., as well as various mixtures thereof and mixtures thereof with water. While each of the above reactions is generally conducted at atmospheric pressure, it is possible to conduct the reaction under reduced pressure as taught by Japanese Unexamined Patent Application KOKAI-62-138478 (1987) to remove the byproduct low-boiling thiol and thereby suppress the secondary reaction. When a low-boiling solvent is used, the reaction is preferably conducted at supratmospheric pressure. For the aforesaid respective reactions, the reaction temperature may range from 30 to 150°C and preferably from 50 to 150°C. The reaction time is generally 5 minutes to 48 hours, depending on the reaction temperature, reactant, reagent and solvent. The proportions of reagents [III] and [V] in the reactions [II]→[IV] and [II]→[VI] may each be 1 to 1.2 molar equivalents relative to [II]. The use of [III] and [V] in further excess is preferably avoided to prevent by-production of the diamino compound. As the reaction [II]→[IV]and [II]→[VI] in a concentrated reaction mixture may occasionally give the by-product, the diamino compound, it is desirable to avoid the reactions in such condition. The proportions of reagents [V]and [III]in the reactions [IV]→[I]and [VI]→[I] are generally 1 to 1.5 molar equivalents and, unlike in the reactions [II]→[IV] and [II]→[VI], the use of [V] or [III] in greater excess may not occasionally induce byproduct formation. A base may be permitted to be concomitantly present for the purpose of promoting the reaction or suppressing secondary reactions. As the base for such purposes, there may be used organic bases such as triethylamine, N-methylmorpholine, pyridine, 1,8-diazabicyclo[5,4,0]-7-undecene, 1,5-azabicyclo[4,3,0]non-5-ene, etc. and inorganic bases such as potassium carbonate, potassium hydrogen carbonate, sodium carbonate, sodium hydrogen carbonate, lithium carbonate, lithium hydrogen carbonate and so on. Where an alkali metal salt of reagent [III] or [V] is used, the sodium salt, lithium salt, potassium salt, etc. can be employed. The compound [IV] or [VI] may be isolated and purified by conventional procedures such as concentration, concentration under reduced pressure, pH adjustment, redistribution, solvent extraction, distillation, crystallization, recrystallization, chromatography, etc. and subjected to the next reaction. Alternatively the reaction mixture containing [IV] or [VI] may be such be directly used as the starting reactant for the next reaction.

The starting compound of general formula [II] for Process 1) can be synthesized by the procedures described in Chem. Ber. 100, 591 (1967), Acta. Chem. Scand. 22, 1107 (1968), Synthesis 1986, 967, Chem. Ber. 95, 2861 (1962), Tetraheron 30, 2413 (1974), Synthesis 1984, 797 and other literature or by procedures analogous thereto. The compound [III] can be synthesized by the procedures described in Organic Functional Group Preparations, Academic Press, Vol 1, Chapter 13 (1968) and Vol 3, Chapter 10 (1972) and other literature or by procedures analogous thereto, and the compound [V] can be synthesized by the procedures described in Survey of Organic Syntheses, Wiley-Interscience (1970), Chapter 8 and other literature or by procedures analogous thereto.

The aforementioned Process 2) comprises (1) reacting an amino compound of general formula [III] (Y = H) or an alkali metal salt (e.g. Na or K salt) with an isothiocyanic ester of general formula [VII] to give a thiourea of general formula [VIII], then reacting said thiourea [VIII] with the compound of the formula: R^5I (e.g. methyl iodide, etc.)to give an isothiourea of general formula [IX], and reacting [IX] with an active methylene compound of general formula [X], (2) reacting an amino compound of general formula [III] (Y = H) or an alkali metal salt thereof with an isothiocyanic ester [VII'], then reacting the resulting thiourea [VIII'] with the compound of the formula: R^5I (e.g. methyl iodide, etc.) to give an isothiourea [IX'] and reacting [IX'] with an active methylene compound [X], or (3) reacting an amino compound of general formula [V](Y = H) or an alkali metal salt thereof with an isothiocyanic acid ester [VII"], reacting the resulting thiourea [VIII"] with the compound of the formula : R^5I (e.g. methyl iodide, etc.), and reacting the resulting isothiourea [IX"] with an active methylene compound, to thereby give the desired compound [I].

Referring to Process 2), the reactions $[III]_{Y=H}$→[VIII], $[III]_{Y=H}$→[VIII'] and $[V]_{Y=H}$→[VIII"] and the reactions [VIII]→[IX], [VIII']→[IX'] and [VIII"]→[IX"] can each be conducted by the known procedures described in the literature or by procedures analogous thereto. As said literature, there may be mentioned Chemical Society of Japan (ed.): Shin Jikken Kagaku Koza (New Series of Experimental Chemistry), Vo. 14, III, Maruzen (1978), Chapters 7 and 21; Organic Functional Group Preparations, Vol. 2, Academic Press (1971), Chapters 6 and 7, ditto The Second Edition (1986), and so on.

Each of the reactions $[III]_{Y=H}$→[VIII], $[III]_{Y=H}$→[VIII'], and $[V]_{Y=H}$→[VIII"] can be conducted in an appropriate solvent. There is no limitation on such a solvent provided that it does not interact with the reactant or the reagent but it is preferable to select a solvent capable of dissolving both the reactant and reagent. As

examples of such solvent, there may be mentioned aromatic hydrocarbons such as benzene, toluene, xylene, etc.; aliphatic hydrocarbons such as pentane, hexane, heptane, petroleum ether, ligroine, petroleum benzene, etc.; ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, dioxane, etc.; acid amides such as dimethylformamide, dimethylacetamide, etc.; sulfoxides such as dimethyl sulfoxide etc.; sulfones such as sulfolane etc.; phosphoramides such as hexamethylphosphoramide etc.; and halogenated hydrocarbons such as chloroform, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, etc. as well as various mixtures thereof. The reaction temperature is about -30° to 200°C and preferably 0 to 150°C. The reaction time varies with such conditions as reaction temperature, reactant, reagent, reaction system concentration and solvent, but generally in the range of 1 minute to 24 hours.

The proportions of compounds [VII], [VII'] and [VII"] required for the respective reactions may range from 0.5 to 2 molar equivalents, preferably 0.8 to 1.2 molar equivalents, relative to $[III]_{Y=H}$, $[III]_{Y=H}$ and $[V]_{Y=H}$. The compounds [VIII], [VIII'] and [VIII"] thus obtained can each be subjected to the next reaction either without isolation or after isolation from the reaction mixture by the known procedure.

Each of the reactions [VIII]→[IX], [VIII']→[IX'] and [VIII"]→[IX"] may also be conducted in a solvent. In addition to the solvents mentioned for the reactions $[III]_{Y=H}$→[VIII], $[III]_{Y=H}$→[VIII'], and $[V]_{Y=H}$→[VIII"], such other solvents as alcohols, e.g. methanol, ethanol, propanol, butanol, etc.; ketones, e.g. acetone, methyl ethyl ketone, etc.; and esters, e.g. methyl acetate, ethyl acetate, butyl acetate, methyl formate, ethyl formate, ethyl propionate, etc. can also be employed. The reagent methyl iodide may be utilized as the solvent. For the purpose of promoting the reaction and minimizing the formation of byproducts, a base may be permitted to be present in the reaction system or permitted to act on the reaction system before or after the reaction and there are cases in which such practice contributes to improved results. As the base that can be used for the above purpose, there may be mentioned sodium hydride, sodium metal, alcoholates such as sodium ethoxide, sodium methoxide, potassium tert-butoxide, etc., organic bases such as triethylamine, diisopropylethylamine, pyridine, N,N-dimethylaniline, etc. and inorganic bases such as potassium carbonate and so on. The proportion of the base is preferably 0.8 to 1.2 molar equivalents relative to [VIII], [VIII'] or [VIII"]. In the absence of a base in the reaction system, [IX], [IX'] or [IX"] is formed as the hydroiodide so that this hydroiodide must be neutralized to obtain [IX], [IX'] or [IX"]. The base for this purpose is preferably a water-soluble inorganic base such as sodium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide and so on. The reaction temperature is 0 to 100°C and preferably 20 to 80°C. The reaction time is generally 0.1 to 24 hours. The proportion of methyl iodide required for the reaction is not less than 1 molar equivalent relative to [VIII], [VIII'] or [VIII"] and may be used in a larger amount as the solvent. The [IX], [IX'] or [IX"] thus produced may be isolated by the conventional procedure before submission to the next reaction or the reaction product mixture may be directly used as the starting material in the next reaction.

Each of the reactions [IX]→[I-1], [IX']→[I-2] and [IX"]→[I-3] can be conducted in accordance with the procedures described in Tetrahedron 37, 1453 (1981) Indian Journal of Chemistry 15B, 297 (1977) and other literature. The reaction may be conducted using the active methylene compound [X] in excess as a solvent or may be carried out in a different solvent. As the solvent just mentioned above, there may be used aromatic hydrocarbons such as benzene, toluene, xylene, etc., aprotic polar solvents such as dimethylformamide, dimethylacetamide, dimethyl sulfoxide, sulfolane, hexamethylphosphoramide, etc., and ethers such as tetrahydrofuran, dioxane and so on. Particularly where an aprotic polar solvent is used and the reaction is conducted under reduced pressure with the byproduct methylmercaptan being dispelled out of the reaction system, the formation of byproducts can be suppressed and the reaction yield improved. The reaction may also be conducted in the presence of a catalyst. As such catalyst, there may be employed zinc chloride, zinc bromide, zinc iodide, cupric chloride and so on. The reaction temperature is 30 to 200°C, preferably 50-150°C. The reaction time is generally 0.1 to 48 hours. The proportion of active methylene compound [X] necessary for the reaction is 1 to 5 molar equivalents relative to [IX], [IX'] or [IX"]. Where [X] is a low-boiling compound, it can be used in a solvent amount.

The starting compounds [VII], [VII'] and [VII"] can be synthesized by the procedures described in Organic Functional Group Preparations, Vol. 1, Academic Press (1968), Chapter 12 and other literature or by procedures analogous thereto, and the compound [X] can be synthesized by procedures described in Formation of C-C Bonds, Vol. 1, Georg Thieme Publishers, Stuttgart (1973) and other literature.

The aforementioned Process 3) comprises reacting a compound [XI] or [XII] with an amino compound of general formula [III] or a salt thereof (e.g. the salt of an alkali metal such as Na or K) and reacting the resulting product further with an amino compound of general formula [V] or a salt (alkali metal salt) thereof or, alternatively, reacting a compound [XI] or [XII] with an amino compound of general formula [V] or a salt thereof and then reacting the resulting product with an amino compound of general formula [III] or a salt thereof to give the desired compound [I].

The reactions in Process 3) can be conducted in the same manner as those in Process 1) and the reaction conditions described for Process 1) can be utilized. However, since compounds [XI] and [XII] are generally more reactive than compound [II], the reactions are preferably conducted under somewhat milder conditions as compared with Process 1).

The compounds [XI] and [XII] can be prepared by procedures described in Chemical Abstracts 44, 1011f, Journal of Organic Chemistry 25, 1312 (1960) and other literature or by procedures analogous thereto.

The aforementioned Process 4) comprises reacting an acid amide of general formula [XIII] or an acid amide of general formula [XV] with a halogenating agent to give a halide of general formula [XIV] or [XVI] and reacting the halide with an amino compound of general formula [V] or a salt thereof or an amino compound of general formula [III] or a salt thereof to give the desired compound [I].

The reaction of [XIII]→[XIV] and that of [XV]→[XVI] are preferably conducted in a solvent. As such solvent, there may be mentioned halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, etc., ethers such as diethyl ether, tetrahydrofuran, dioxane, etc., nitriles such as acetonitrile, propionitrile, etc. and so on. This reaction is preferably carried out under anhydrous conditions. The halogenating agent may for example be phosphorus pentachloride, hosphorus oxychloride, phosphorus trichloride, thionyl chloride, oxalyl chloride or the like. The proportion of the halogenating agent is 1 to 10 molar equivalents, preferably 1 to 5 molar equivalents, relative to [XIII] or [XV]. Preferably a base is permitted to be present in the reaction system in order to trap the byproduct hydrogen chloride, and as such base, there may be used various organic bases such as pyridine, triethylamine, diisopropylethylamine, N-methylmorpholine, N,N-dimethylaniline, N,N-diethylamine and so on. The reaction temperature is -80° to 100°C and preferably -50° to 50°C. The reaction time is generally 0.1 to 24 hours, depending on the reactant, base, solvent, reaction concentration and reaction temperature. The products [XIV] and [XVI] can be isolated and purified by the aforementioned known procedures before submission to the next reaction or the reaction product mixture may be directly used in the next reaction.

The reaction of [XIV]→[I] and that of [XVI]→[I] can each be conducted in a solvent similar to those mentioned for the reactions of [XIII]→[XIV] and [XV]→[XVI], preferably under anhydrous conditions. The proportion of [V] or a salt thereof and that of [III] or a salt thereof are 1 to 10 molar equivalents, preferably 1 to 5 molar equivalents, relative to [XIV] and [XVI], respectively. For the purpose of trapping the byproduct hydrogen chloride, [V] or a salt thereof or [III] or a salt thereof can be used in excess but for economy, a different base is preferably permitted to be present. A such base, there may be used any of the bases mentioned for the reactions of [XIII]→[XIV] and [XV]→[XVI]. The reaction temperature is -80°C to 100°C and preferably -50°C to 50°C. The reaction time is generally 0.1 to 24 hours. The starting compounds [XIII] and [XV] can be synthesized by the procedures described in Formation of C-C Bonds, Vol. 1, Georg Thieme Publishers, Stuttgart (1973) and Chemical Society of Japan(ed.): 'Shin Jikken Kagaku Koza' (New Series of Experimental Chemistry), Vol. 14,II, Maruzen (1977), Chapters 5 and 7 and other literature or by procedures analogous thereto.

The aforementioned Process 5) comprises reacting a compound of general formula [XVII] with a halide of general formula [XVIII] to give the desired compound [I].

The reaction according to Process 5) is preferably conducted in an appropriate solvent. As such solvent, there may be employed acid amides such as dimethylformamide, dimethylacetamide, etc., sulfoxides such as dimethyl sulfoxide etc., sulfones such as sulfolane etc., phosphoramides such as hexamethylphosphoramide etc., ethers such as tetrahydrofuran, dioxane, 1,2-dimethoxyethane, diethylene glycol dimethyl ether, etc., and so on. Mixtures of such solvents may likewise be employed. This reaction is preferably conducted in the presence of a base. As such base, there may be mentioned sodium hydride, potassium hydride, lithium hydride, calcium hydride, n-butyllithium, lithium diisopropylamide, sodium amide and so on. It is preferable that the compound [XVII] be converted to the salt of said base before it is subjected to the reaction. The proportion of the base is preferably 1 to 1.5 molar equivalents relative to [XVII]. This reaction is preferably conducted under anhydrous conditions and may be carried out in an atmosphere of nitrogen gas or argon gas. The proportion of [XVIII] is 1 to 2 molar equivalents, preferably 1 to 1.5 molar equivalents, relative to [XVII]. The reaction temperature is -70°C to 150°C and preferably -50°C to 100°C. The reaction time is generally 0.1 to 48 hours.

The compound [XVII] can be easily prepared, for example by using a compound of general formula R^2NH_2 wherein R^2 has the meaning defined hereinbefore, instead of compound [III] in said Processes 1 through 4). The compound [XVIII] can be synthesized by the process described in Organic Functional Group Preparations, Vol. 1, Academic Press (1968), Chapter 6 and other literature or by procedures analogous thereto.

The aforementioned Process 6) comprises subjecting a compound of general formula [XIX], which falls within the category of compound [I], to hydrolysis reaction and, then, to decarboxylation reaction to give a compound of general formula [I-4] which falls within the category of compound [I].

The above hydrolysis reaction can be conducted under the conditions of hydrolysis of esters which are known in the art.

Thus, in a solvent (inclusive of a solvent mixture) such as water, alcohols (e.g. methanol, ethanol, propanol, butanol, diethylene glycol, 2-methoxyethanol, etc.), ketones (e.g. acetone etc.), ethers (e.g. tetrahydrofuran, dioxane, dimethoxyethane, etc.), amides (e.g. dimethylformamide, dimethylacetamide, hexamethylphosphoramide, etc.), sulfoxides (e.g. dimethyl sulfoxide etc.), sulfones (e.g. sulfolane etc.) and carboxylic acids (e.g. formic acid, acetic acid, etc.), the hydrolysis reaction can be conducted using an acid (for example, mineral acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, etc., organic acids such as p-toluenesulfonic acid etc., strongly acidic ion exchange resins, and so on) or a base (for example, sodium hydroxide, potassium hydroxide, potassism carbonate, sodium hydrogen carbonate, barium hydroxide, calcium hydroxide, sodium methoxide, ammonia and so on), although the use of a base is preferred. The proportion of the base is about 1 to 10 molar equivalents, preferably about 1.2 to 4 molar equivalents, relative to [XIX]. The reaction temperature is about -20 °C to 200 °C, preferably about -5 °C to 120 °C, and the reaction time is about 0.1 to 48 hours, preferably about 0.1 to 24 hours.

The decarboxylation reaction proceeds simultaneously with said hydrolysis reaction in many cases and usually no special procedure is required. If necessary, this reaction may be carried out by heating in the hydrolysis solvent. The reaction temperature is generally about 0 to 200 °C, preferably 30 to 150 °C, and the reaction time is 0.1 to 48 hours and preferably 0.1 to 24 hours.

The aforementioned Process 7) comprises subjecting a compound of general formula [I-5] or a compound of general formula [I-6] to alkylation, acylation, alkoxycarbonylation, sulfonylation or phosphorylation to give a compound [I].

For alkylation, the amino group in [I-5] or [I-6] is alkylated with an alkylating agent such as an alkyl chloride, alkyl bromide, alkyl iodide, dialkyl sulfate or the like. The proportion of the alkylating agent is about 1 to 3 equivalents relative to the starting compound in many instances. This alkylation reaction may be conducted under the same conditions as those described for Process 5).

The acylation, sulfonylation, phosphorylation and alkoxycarbonylation reaction can each be conducted by procedures known per se or by procedures analogous thereto.

The acylating agent for said acylation reaction may for example be an acyl halide or acid anhydride containing a group of R^1 or R^2. The sulfonylating agent for said sulfonylation reaction may for example be a sulfonyl halide or sulfonic anhydride containing a group of R^1 or R^2. The alkoxycarbonylating agent for said alkoxycarbonylation reaction may for example an alkoxycarbonyl halide or carbonate containing a group of R^1 or R^2. The preferred halogens in the above-mentioned halide reagents are bromine and chlorine. The proportion of each such reagent is at least one molar equivalent, preferably about 1 to 5 molar equivalents, relative to the starting compound. Where an acid anhydride is used as the acylating agent in the above acylation reaction, it can be employed in excess. These reactions are carried out in a solvent capable of dissolving the compound [I-5] or [I-6] and the respective reagents and as preferred examples of such solvent, there may be mentioned dichloromethane, chloroform, dichloroethane, tetrahydrofuran, dioxane, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, hexamethylphosphorotriamide, pyridine and so on. The reaction temperature is about -50 °C to 150 °C and the reaction time is about 0.1 to 48 hours. The reaction may be hastened and the secondary reactions suppressed to improve the yield when the reaction is conducted in the concomitant presence of an amine such as triethylamine, dimethylaminopyridine, pyridine, N,N-dimethylaniline, N,N-diethylaniline, etc., sodium hydride, potassium hydride, sodium amide, n-butyllithium, lithium diisopropylamide or the like.

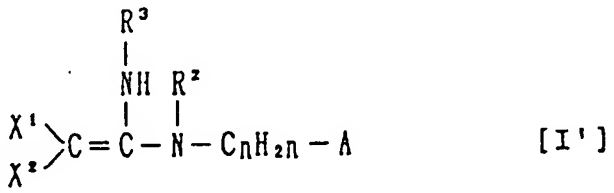
The object compound [I] or salt thereof thus produced can be isolated and purified by conventional procedures such as concentration, concentration under reduced pressure, distillation, fractional distillation, pH adjustment, redistribution, solvent extraction, crystallization, recrystallization, chromatography and so on.

Where the compound [I] is obtained as the free compound, it can be converted to an agrochemically useful salt and where a salt is obtained, it can converted to the free compound [I], using the conventional procedure in either case. Where the compound [I] contains acidic groups such as carboxyl, sulfo and/or phosphono groups in its positions X^1, X^2, R^1, R^2 and/or A, it may form a salt with a base. As the base used for this purpose, there may be mentioned inorganic bases such as sodium, potassium, lithium, calcium, magnesium, ammonia, etc. and organic bases such as pyridine, collidine, triethylamine, triethanolamine and so on. Where the compound [I] contains basic groups such as amino, substituted amino and/or other groups in its positions X^1, X^2, R^1, R^2 and/or A, it can form an acid addition salt. As examples of such acid addition salts, there may be mentioned hydrochloride, hydrobromide, hydroiodide, nitrate, sulfate, phosphate,

acetate, benzoate, maleate, fumarate, succinate, tartarate, citrate, oxalate, glyoxalate, aspartate, methanesulfonate, methanedisulfonate, 1,2-ethanedisulfonate, benzenesulfonate and so on.

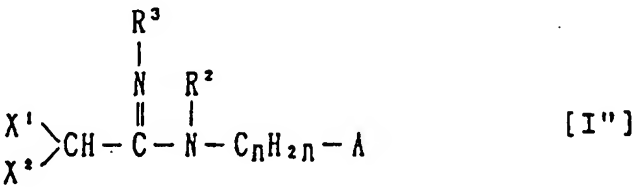
The compound [I] may form an inner salt, which also falls within the scope of the invention.

The compound [I] and its stereoisomer and tautomer (for example, where the compound [I] is a compound of the formula



[I']

wherein the symbols have the meanings defined hereinbefore, its tautomer of the formula



[I"]

wherein the symbols have the meanings defined hereinbefore, also falls into the category of compound [I]) can be used, either independently or in the form of a mixture, as an insecticidal/miti(acari)cidal agent.

The compound [I] and its salt according to the invention are effective in the control of household pests and animal or plant parasitizing insects and mites, and exhibit strong pesticidal effects as a contact poison when applied directly to the host animals and plants. The most salient feature of the compound, however, is that it displays potent pesticidal effects even after it has been absorbed into plants via the root, leaf, stem or the like and come into contact with the pests as the pests suck or gnaw on the plants. This property is advantageous in the control or sucking/biting insects and ticks. Furthermore, the compound of the invention is of low toxicity to plants and fish, thus having safe and useful characteristics as an agricultural pesticide.

The compound [I] and its salts and compositions containing the same are particularly effective in the control of the following kinds of pests: pests of the order Hemiptera such as Eurydema rugosum, Scotinophara lurida, Riptortus clavatus, Stephanitis nashi, Laodelphax striatellus, Nilaparvata lugens, Nephotettix cincticeps, Unaspis yanonensis, Aphis glycines, Lipaphis erysimi, Brevicoryne brassicae, Aphis gossypii, Sogattela furcifera, Nezara viridula, Trialeurodes vaporariorum, Myzus persicae, Pseudococcus comstocki, Aphis promi, Nezara spp., Cimex lectularius, Psylla spp., etc.; pests of the order Lepidoptera such as Spodoptera litura, Plutella xylostella, Pieris rapae crucivora, Chilo suppressalis, Plusia nigrisigna, Halicoverpa assulta, Leucania separata, Mamestra brassicae, Adoxophyes orana, Notarcha derogata, Cnaphalocrocis medinalis, Phthorimaea operculella, etc.; pests of the order Cleoptera such as Epilachna vigintioctopunctata, Aulacophora femoralis, Phyllotreta striotata, Oulema oryzae, Echinocnemus squameus, etc; pests of the order Diptera such as Musca domestica, Culex pipiens pallens, Tabanus trigonus, Hylemyia antiqua, Hylemyia platura etc.; pests of the order Orthoptera such as Locusta migratoria, Gryllotalpa africana, etc., cockroaches such as Blattella germanica, Periplaneta fuliginosa, etc.; spider mites such as Tetranychus urticae, Panonychus citri, Tetranychus kanzawai, Tetranychus cinnabarinus, Panonychus ulmi, Aculops pelekassi , etc., and nematodes such as Aphelenchoides besseyi and so on.

For application of the compound [I] or salt of the invention as an insecticide/miti(acari)cide, it can be formulated into any possible and desired application form for agrochemicals. Thus, by dissolving or dispersing one or more species of compound [I] and salt thereof in an appropriate liquid carrier or vehicle or admixing them with or causing them adsorbed on an appropriate solid carrier, an emulsifiable concentrate, oil preparation, wettable powders, dusts, granules, tablets, aerosol, ointment or the like can be manufactured. If necessary, such compositions may be further supplemented with emulsifiers, suspending agents, spreader-stickers, penetrating agents, wetting agents, thickeners, stabilizers and so on, and any of such preparations can be manufactured by the per se known procedures.

The concentration of the active ingredient (compound [I] or salt thereof) in such an insecticidal/miti-(acari)cidal composition of the invention depends on the intended application. Generally speaking, the

proper concentration is about 10 to 90 weight percent for emulsifiable concentrate and wettable powders, about 0.1 to 10 weight percent for oils and dusts and about 1 to 20 weight percent for granules, for instance. However, the concentration may be adjusted according to the intended application. In the case of an emulsifiable concentrate or a wettable powder, it is diluted with water or the like to a suitable concentration (for example, 100 to 100,000-fold dilution) before spraying.

The liquid carrier (solvent) includes, among others, water, alcohols (e.g. methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, ethylene glycol, etc.), ketones (e.g. acetone, methyl ethyl ketone, etc.), ethers (e.g. dioxane, tetrahydrofuran, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, propylene glycol monomethyl ether, etc.), aliphatic hydrocarbons (e.g. kerosin, kerosene, fuel oil, machine oil, etc.), aromatic hydrocarbons (e.g. benzene, toluene, xylene, solvent naphtha, methylnaphthalene, etc.), halogenated hydrocarbons (e.g. methylene chloride, chloroform, carbon tetrachloride, etc.), acid amides (e.g. dimethylformamide, dimethylacetamide, etc.), esters (e.g. ethyl acetate, butyl acetate, fatty acid glycerin esters, etc.), nitriles (e.g. acetonitrile, propionitrile, etc.) and so on. One of these solvents or a mixture of two or more of them can be used as the carrier.

The solid carrier (diluent-volume builder) includes, among others, vegetable powders (e.g. soybean flour, tobacco flour, wheat flour, sawdust, etc.), mineral powders (e.g. clays such as kaolin, bentonite, acid clay, etc., talcs such as talc, pyrophillite, etc.
and silicates such as diatomaceous earth, mica powder, etc.), alumina, sulfur powder, activated carbon and so on. These powders can be used singly or as a mixture.

The ointment base that can be employed include, among others, any or a mixture of polyethylene glycol, pectin, higher fatty acid polyhydric alcohol esters such as monostearic acid glycerin ester etc., cellulose derivatives such as methylcellulose etc., sodium alginate, bentonite, higher alcohols, polyhydric alcohols such as glycerin, vaseline, white petrolatum, liquid paraffin, lard, vegetable oils, lanolin, anhydrous lanolin, hydrogenated oils, resins, etc., or mixtures thereof with the any of the following surfactants.

Surfactants which can be optionally used as said emulsifier, spreader/sticker, penetrating agent, dispersing agent, etc. include soaps and nonionic or anionic surfactants such as polyoxyethylene alkyl aryl ethers (e.g. Noigen, E.A. 142®, manufactured by Daiichi Kogyo Seiyaku Co., Ltd., JAPAN; Nonal®, Toho Chemical, JAPAN), alkylsulfates (e.g. Emal 10®, Emal 40®, manufactured by Kao Corporation, JAPAN), alkylsulfonates (e.g. Neogen®, Neogen T®, manufactured by Daiichi Kogyo Seiyaku Co., Ltd.; Neopellex®, manufactured by Kao Corporation), polyethylene glycol ethers (e.g. Nonipol 85®, Nonipol 100®, Nonipol 160®, manufactured by Sanyo Chemical Industries, Ltd., JAPAN) and polyhydric alcohol esters (e.g. Tween 20®, Tween 80®, manufactured by Kao Corporation).

The compound of the invention can be used in combination with other insecticides (pyrethroid insecticides, organophosphorus insecticides, carbamate insecticides, natural insecticides, etc.), miticides (acaricides), nematocides, herbicides, plant hormones, plant growth regulators, fungicides (copper fungicides, organochlorine fungicides, organosulfur fungicides, phenolic fungicides, etc.), synergists, attractants, repellents, pigments, fertilizers and so on.

The resulting insecticide /miticide according to the invention is of low toxicity and safe and is an excellent agrochemical. The insecticidal/miticidal agent of the invention can be used in the same manner as the conventional insecticides and miticides and produces effects surpassing those of the latter. For example, the insecticidal/miticidal agent of this invention can be applied for control of pests by such procedures as nursery bed treatment, stem/foliage spray or dusting, direct application to pests, paddy water treatment, soil treatment and so on. The dosage can be selected from a broad range according to the timing, site and method of application. Generally speaking, the preferred dosage of the active ingredient (compound [I] or a salt thereof) per hectare is 0.3 g to 3,000 g and, for still better results, 50 g to 1,000 g. Where the insecticidal/miticidal agent of the invention is provided as a wettable powder, it can be used as diluted so that the final concentration of the active ingredient will be in the range of 0.1 to 1,000 ppm, preferably 10 to 500 ppm.

The compound [I] of the invention has excellent insecticidal/miticidal activity which is well demonstrated by the following test examples.

Test Example 1

Effect against brown planthoppers (Nilaparvata lugens)

An emulsifiable concentrate of the compound of the invention, prepared in the same manner as Example 112 below, was diluted with water to a concentration of 500 ppm and sprayed over the stems and leaves of rice seedlings in the 2-leaf stage at the rate of 10 ml per paper pot. Water was put in test tubes

and the treated rice seedlings were placed therein. Then, 10 brown planthopper larvae were released in each tube, which was then capped with an aluminum cap. The test tubes were maintained in an incubator at 25 °C and the dead insects were counted 7 days after release. The % mortality was calculated using the following formula.

$$\text{Mortality (\%)} = \frac{\text{Number of dead insects}}{\text{Number of insects released}} \times 100$$

The results are shown in Table 1.

Table 1 Effect against brown planthoppers

Compound of the invention (Compound No.)	% Mortality after 7 days
3	100
4	100
7	100
12	100
14	100
17	100
18	100
19	100
20	100
24	100
25	100
26	100
28	100
29	100
31	100
32	100
33	100
34	100
35	100
37	100
38	100
40	100
41	100
42	100
43	100
44	100
45	100
46	100
47	100
49	100
50	100
51	100
52	100
55	100

Compound of the invention (Compound No.)	% Mortality after 7 days)
56	100
57	100
58	100
59	100
60	100
61	100
62	100
64	100
65	100
67	100
68	100
70	100
71	100
72	100
73	100
75	100
76	100
77	100
78	100
79	100
80	100
84	100
85	100
86	100
88	100
89	100
90	100
91	100
92	100
93	100
95	100
96	100
97	100
98	100
99	100
100	100
101	100
102	100
103	100
104	100
105	100
106	100
107	100
108	100
109	100
110	100
111	100

Compound of the invention (Compound No.)	% Mortality after 7 days
112	100
113	100
mixture (7:3) of 114 and 115	100
116	100
117	100
118	100
mixture (90:10) of 119 and 120	100
mixture (40:60) of 119 and 120	100
121	100
122	100
mixture (70:30) of 123 and 124	100
124	100
125	100
126	100
127	100
128	100
129	100
130	100
131	100

It is apparent from Table 1 that the compound [I] of the invention has excellent pesticidal activity against brown planthoppers.

The following reference and working examples are further illustrative of the invention but should by no means be construed as limiting the scope of the invention.

In the procedures of column chromatography described in the reference and working examples, elution was carried out under monitoring by thin layer chromatography (TLC). For TLC observation, Merck Kieselgel 60 F_{254} (Art. 5715) was used as the TLC plate, the column chromatographic eluent as the developing solvent, and the UV detector as the means of detection. As the silica gel for column packing, Merck Kieselgel 60 (70-230 mesh, Art. 7734) was used. The NMR data represent ^{1}H-NMR spectra determined using tetramethylsilane as either an internal or an external standard and, unless otherwise indicated, a Varian EM390 (90 MHz) spectrometer. The NMR data carrying the indication of 400 MHz were generated using a JEOL GX-400 (400 MHz) spectrometer. All the δ data are in ppm. Where a solvent mixture was used as the developer or eluent, the ratio of respective solvents is given in parentheses.

The abbreviations used in the reference and working examples have the following meanings.

Me: methyl; nPr: n-propyl, iPr: isopropyl, Et: ethyl, Ac: acetyl, s: singlet, br: broad, d: doublet, t: triplet, q: quartet, m: multiplet, dd: doublet doublet, tt: triplet triplet, dt: doublet triplet, td: triplet doublet, ddd: doublet doublet doublet, S + S: two singlets, J: coupling constant, Hz: hertz, $CDCl_3$: chloroform-d, D_2O: deuterium oxide, DMSO-d_6: dimethyl-d_6 sulfoxide, %: weight %, m.p. : melting point.

Reference Example 1

N-Methyl-N-3-pyridylmethylamine

To 25 ml of a 20% aqueous solution of NaOH stirred under cooling with ice-water, a 40% aqueous solution of methylamine (13.6 g, 0.175 mole) was added dropwise over 5 minutes, followed by further dropwise addition of an aqueous solution (10 ml) of 8.2 g (0.05 mole) of 3-pyridylmethyl chloride hydrochloride over 10 minutes. The mixture was further stirred at room temperature for 2 hours and, then, extracted with CH_2Cl_2 (100 ml x 3). The extract was dried over $MgSO_4$ and distilled to remove the solvent. The residue was subjected to vacuum distillation to give 2.6 g of the title compound as a yellow oil.

b.p.: 66 °C/2 mmHg
NMR ($CDCl_3$) δ: 1.48 (s, NH), 2.45 (s, NMe), 3.76 (s, CH_2N)

Reference Example 2

N-(6-Chloro-3-pyridylmethyl)phthalimide

In 20 ml of EtOH, 9.4 g (6.4 x 10^{-2} mole) of phthalimide and 4.2 g of KOH were stirred for 30 minutes, followed by addition of 100 ml of DMF (dimethylformamide) and 5.2 g (2.5 x 10^{-2} mole) of 6-chloro-3-pyridylmethyl chloride. The mixture was stirred at 60 °C for 1 hour. The EtOH and DMF were distilled off under reduced pressure and the residue was chromatographed on a silica gel column and eluted with CH_2Cl_2. The above procedure gave 6.7 g of the title compound as colorless needles.
m.p.: 142-143 °C
NMR ($CDCl_3$) δ: 4.85 (s, 2 H), 7.28 (d, J = 8.9 Hz, 1 H), 7.6-8.0 (m, 5 H), 8.51 (d, J = 2.8 Hz, 1 H)

Reference Example 3

6-Chloro-3-pyridylmethylamine

Hydrazine hydrate (1.7 ml) was added to a refluxing solution of 6.5 g (2.4 x 10^{-2} mole) of N-(6-chloro-3-pyridylmethyl)phthalimide in 100 ml of EtOH, and the mixture was further refluxed for 1 hour. After addition of 20 ml of water, the ethanol was distilled off under reduced pressure. Concentrated hydrochloric acid (25 ml) was added to the residue and the mixture was refluxed for 1 hour. After cooling, the reaction mixture was neutralized with NaOH and the aqueous layer was saturated with NaCl and extracted with Et_2O. The extract was dried over Na_2SO_4 and the solvent was distilled off to give 2.4 g of the title compound as a yellow oil.
NMR ($CDCl_3$) δ: 1.4-2.0 (br, 2 H), 3.89 (s, 2 H), 7.27 (d, J = 8.9 Hz, 1 H), 7.67 (dd, J = 8.9 & 2.7 Hz, 1 H), 8.32 (d, J = 2.7 Hz, 1 H)

Reference Example 4

1-Methylthio-1-piperidino-2-nitroethylene

In 20 ml of EtOH was dissolved 1.7 g (0.01 mole) of 1,1-bis(methylthio)-2-nitroethylene under heating and 0.9 g (0.01 mole) of piperidine dissolved in 10 ml of EtOH was added dropwise in 3 portions at 30-minutes intervals under reflux. After 2 hours of reflux, the solvent was distilled off and the residue was chromatographed on a silica gel column and eluted with AcOEt-toluene (2:3). The above procedure yielded 0.8 g of the title compound as yellow prisms.
m.p.: 65-67 °C
NMR ($CDCl_3$) δ: 2.45 (s), 6.68 (s)
IR (Nujol): 1650, 1530, 1380 cm^{-1}

Reference Example 5

1,1-bis(Methylthio)-2-nitroethylene was reacted with various amines in the same manner as Reference Example 4 to give the following compounds.

(1) 1-Methylamino-1-methylthio-2-nitroethylene (yellow scales)
m.p.: 111-112 °C
NMR ($CDCl_3$) δ: 2.45 (s), 3.15 (d), 6.62 (s), 10.5 (br s)
IR (Nujol): 3200, 1575, 1345 cm^{-1}
(2) 1-(2,2-Dimethyl-1-hydrazino)-1-methylthio-2-nitroethylene (pale yellow prisms)
m.p.: 139-140 °C
NMR ($CDCl_3$) δ: 2.26 (s), 2.65 (s), 6.40 (s), 10.46 (br s)
IR (Nujol): 3130, 1535, 1340 cm^{-1}

Reference Example 6

N-(6-Chloro-3-pyridylmethyl)-N-methylamine

(1) In 30 ml of toluene, 0.8 g (5.7×10^{-3} moles) of 6-chloropyridine-3-aldehyde and 10 g of Na_2SO_4 were mixed and while the mixtures was stirred, a 40% aqueous solution of methylamine (1.4 g, 1.1×10^{-2} mole) was added dropwise over 30 minutes, followed by addition of 10 g of $MgSO_4$. The mixture was allowed to stand at room temperature overnight, after which it was filtered. The filtrate was concentrated to give 0.6 g (yield 68%) of N-(6-chloro-3-pyridylmethylidene)methylamine as crystals.

NMR ($CDCl_3$) δ: 3.52 (d, 3 H), 7.35 (d, J = 8.8 Hz, 1 H), 8.04 (dd, J = 8.8 & 2.7 Hz, 1 H), 8.2-8.4 (m, 1 H), 8.59 (d, J = 2.7 Hz, 1 H)

(2) In 10 ml of MeOH was dissolved 0.6 g (3.8×10^{-3} moles) of the N-(6-chloro-3-pyridylmethylidene)-methylamine obtained in (1) and under stirring at 0 °C, 0.07 g (1.9×10^{-3} mole) of sodium borohydride was added in small portions. After 30 minutes, MeOH was distilled off and the residue was diluted with 5 ml of water and extracted with AcOEt (10 ml x 3). The extract was dried over $MgSO_4$ and concentrated to give 0.43 g (yield 71%) of the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 1.90 (s, 1 H), 2.44 (s, 3 H), 3.74 (s, 2 H), 7.28 (d, J = 8.2 Hz, 1 H). 7.67 (dd, J = 8.2 & 2.8 Hz, 1 H), 8.31 (d,J = 2.8 Hz, 1 H)

Reference Example 7

Pyridine-3-aldehyde or quinoline-3-aldehyde was reacted with various amines or 1,1-dimethylhydrazine in the same manner as Reference Example 6 (1) to give the following compounds.

(1) N-(3-Pyridylmethylidene)ethylamine (pale yellow oil)
NMR ($CDCl_3$) δ : 1.30(t), 3.66(q), 8.31(s)

(2) N-(3-Pyridylmethylidene)-2-dimethoxyethylamine (yellow oil)
NMR ($CDCl_3$) δ: 3.43 (s), 3.83 (d), 4.71 (t), 8.35 (s)

(3) N-(3-Pyridylmethylidene)-2-methoxyethylamine (pale yellow oil)
NMR ($CDCl_3$) δ: 3.39 (s), 3.76 (m), 8.36 (s)

(4) N-(3-Quinolylmethylidene)methylamine (yellow oil)
NMR ($CDCl_3$) δ: 3.53 & 3.54 (each s, =NMe), 7.1-8.5 (m, 6H, quinoline-H_6), 9.28 & 9.30 (each s, CH = N)
IR (neat): 1690, 1645, 1615, 1490, 785, 750 cm^{-1}

(5) 1,1-Dimethyl-2-(3-pyridylmethylidene)hydrazine (colorless oil)
b.p.: 110 °C/2 mmHg
NMR ($CDCl_3$) δ: 3.00 (s, NMe_2), 7.15 (s, CH = N)
IR (neat): 1580, 1550, 1465, 1415, 1040, 710 cm^{-1}

(6) N-(3-Pyridylmethylidene)-n-propylamine (pale yellow oil)
NMR ($CDCl_3$) δ: 0.95 (t), 1.75 (m), 3.62 (t), 7.33 (dd), 8.12 (dt), 8.31 (s, CH = N), 8.62 (dd), 8.86 (d)

(7) N-(3-Pyridylmethylidene)-n-butylamine (pale yellow oil)
NMR ($CDCl_3$) δ: 0.94 (t), 1.20-1.90 (m), 3.65 (t), 7.33 (dd), 8.12 (dt), 8.31 (s, CH = N), 8.62 (dd), 8.86 (d)

(8) N-(3-Pyridylmethylidene)benzylamine (pale yellow oil)
NMR ($CDCl_3$) δ: 4.84 (s, CH_2), 7.33 (s, C_6H_5), 7.33 (dd), 8.15 (dt), 8.40 (br s, CH = N), 8.65 (dd), 8.88 (d)

Reference Example 8

The compounds of Reference Example 7 (1)-(4) and (6)-(8) were respectively reacted in the same manner as Reference Example 6 (2) to give the following compounds.

(1) N-Ethyl-N-(3-pyridylmethyl)amine (pale yellow oil)
b.p.: 60 °C/0.7 mmHg
NMR ($CDCl_3$) δ: 1.13 (t), 1.45 (br s), 3.70 (q), 3.82 (s)

(2) N-(2-Dimethoxyethyl)-N-(3-pyridylmethyl)amine (yellow oil)
NMR ($CDCl_3$) δ: 1.73 (br s), 2.75 (d), 3.36 (s), 3.82 (br s), 4.46 (t)

(3) N-(2-Methoxyethyl)-N-(3-pyridylmethyl)amine (colorless oil)
b.p.: 90 °C/0.7 mmHg
NMR ($CDCl_3$) δ: 1.86 (br s), 2.82 (t), 3.36 (s), 3.53 (t), 3.83 (s)

(4) N-Methyl-N-(3-quinolylmethyl)amine (yellow oil)
NMR ($CDCl_3$) δ: 2.24 (s, NMe), 3.09 (br, NH), 3.86 (s, NCH_2), 7.3-8.2 (m, 5 H, quinoline-H_5), 8.83 (d, J = 2 Hz, 1 H, quinoline-H_1)
(5) N-(n-Propyl)-N-(3-pyridylmethyl)amine (yellow oil)
b.p.: 85 °C/1.5 mmHg
NMR ($CDCl_3$) δ: 0.90 (t), 1.30-1.76 (m), 1.64 (br s, NH), 2.60 (t), 3.80 (s), 7.23 (dd), 7.67 (dt), 8.43-8.63 (m)
(6) N-(n-Butyl)-N-(3-pyridylmethyl)amine (pale yellow oil)
b.p.: 83 °C/1 mmHg
NMR ($CDCl_3$) δ: 0.78-1.06 (m), 1.1-1.75 (m), 1.45 (br s, NH), 2.63 (t), 3.80 (s), 7.24 (dd), 7.69 (dt), 8.46-9.63 (m, 2 H)
(7) N-Benzyl-N-(3-pyridylmethyl)amine (colorless oil)
b.p.: 125 °C/0.5 mmHg
NMR ($CDCl_3$) δ: 1.83 (br s, NH), 3.77 (s, 4 H), 7.26 (dd), 7.32 (br s, C_6H_5), 7.66 (dt), 8.43-8.60 (m, 2 H)

Reference Example 9

1,1-Dimethyl-2-(3-pyridylmethyl)hydrazine

In 100 ml of dry ethyl ether was suspended 4.6 g of lithium aluminum hydride and with stirring in a nitrogen gas stream, a solution of 12.0 g of 1,1-dimethyl-2-(3-pyridylmethylidene)hydrazine in 50 ml of dry ethyl ether was added dropwise. The mixture was refluxed for 5 hours and, then, cooled (5 °C) and with stirring, 5 ml of water, 5 ml of 20% aqueous sodium hydroxide and 15 ml of water were added dropwise in succession. The insoluble matter was filtered off, the filtrate was concentrated, and the residue was purified by silica gel column chromatography (eluent: chloroformethanol = 10:1). The resulting oil was distilled under reduced pressure to give 2.5 g of the title compound as a yellow oil.
b.p: 100-115 °C/1 mmHg
NMR ($CDCl_3$) δ: 2.47 (s, NMe_2), 2.81 (br s, NH), 3.93 (s, CH_2N)

Reference Example 10

2,6-Dichloro-3-pyridylmethylamine

(1) In 40 ml of DMF was suspended 3.9 g (0.021 mole) of potassium phthalimide followed by addition of 3.9 g (0.02 mole) of 2,6-dichloro-3-pyridylmethyl chloride and the mixture was stirred at 60-70 °C for 2 hours. The DMF was distilled off under reduced pressure and the residue was diluted with 50 ml of water and extracted with $CHCl_3$ (50 ml x 3). The extract was dried over $MgSO_4$ and concentrated and the resulting precipitate was collected by filtration, washed with ether and dried to give 3.8 g of N-2,6-dichloro-3-pyridylmethyl)phthalimideas white prisms.
m.p.: 189-190 °C
NMR ($CDCl_3$) δ: 4.95 (s, 2 H), 7.22 (d, J = 8.5 Hz), 7.65 (d, J = 8.5 Hz), 7.66-8.0 (m, 4 H)
(2) In a mixture of 50 ml EtOH and 20 ml DMF was dissolved 3.1 g (0.01 mole) of N-(2,6-dichloro-3-pyridylmethyl)phthalimide under heating, followed by addition of 0.75 g (0.015 mole) of $H_2NNH_2 \cdot H_2O$ under reflux. After 1 hour of refluxing, EtOH and DMF were distilled off. To the residue were added 10 ml of concentrated hydrochloric acid and 5 ml of water, and the mixture was refluxed for 30 minutes. The resulting crystals were filtered off and the filtrate was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (30 ml x 3). The extract was dried over $MgSO_4$ and the solvent was distilled off to give 1.45 g of the title compound as a yellow oil.
NMR ($CDCl_3$) δ: 1.55 (s, 2H), 3.96 (s, 2H), 7.27 (d, J = 8.5 Hz), 7.82 (d, J = 8.5 Hz)

Reference Example 11

N-(2,6-Dichloro-3-pyridylmethyl)-N-methylamine

In 50 ml of acetonitrile was dissolved 7.8 g (0.1 mole) of 40% aqueous methylamine and with stirring and ice-cooling, a solution of 3.9 g (0.02 mole) of 2,6-dichloro-3-pyridylmethyl chloride in 10 ml of acetonitrile was added dropwise over 5 minutes. After completion of the dropwise addition, the mixture was

stirred at room temperautre for 2 hours and, then, concentrated. The residue was extracted with ether (30 ml x 3) and dried over $MgSO_4$. Finally, the solvent was distilled off to give 3.2 g of the title compound as a pale yellow oil.

NMR ($CDCl_3$) δ: 1.46 (s, NH), 2.46 (s, 3 H), 3.82 (s, 2 H), 7.26 (d, J = 8.5 Hz), 7.75 (d, J = 8.5 Hz)

Reference Example 12

1-[N-(2,6-Dichloro-3-pyridylmethyl)-N-methyl]amino-1-methylthio-2-nitroethylene

The reaction according to Reference Example 4 was repeated except that N-(2,6-dichloro-3-pyridylmethyl)-N-methylamine was used in lieu of piperidine. The procedure gave the title compound as yellow prisms.

m.p.: 111-112 °C

NMR ($CDCl_3$) δ: 2.46 (s, 3 H), 3.12 (s, 3 H), 4.84 (s, 2 H), 6.79 (s, 1 H), 7.35 (d, J = 8.5 Hz), 7.66 (d, J = 8.5 Hz)

Reference Example 13

1,1-bis(Methylthio)-2-nitroethylene was reacted with various amines in the same manner as Reference Example 4 to give the following compounds.

(1) 1-Dimethylamino-1-methylthio-2-nitroethylene (yellow oil)

NMR ($CDCl_3$) δ: 2.46 (s, 3 H), 3.21 (s, 6 H), 6.69 (s, 1 H)

(2) 1-(N-Ethyl-N-methyl)amino-1-methylthio-2-nitroethylene (yellow oil)

NMR ($CDCl_3$) δ: 1.27 (t, J = 6.5 Hz, 3 H), 2.48 (s, 3 H), 3.13 (s, 3 H), 3.64 (q, J = 6.5 Hz, 2 H), 6.73 (s, 1 H)

(3) 1-(4-Chlorobenzyl)amino-1-methylthio-2-nitroethylene (pale yellow crystals)

m.p.: 121-123 °C

NMR ($CDCl_3$) δ: 2.43 (s, Me), 4.60 (d, J = 6 Hz, CH_2), 6.59 (s, $=CHNO_2$), 7.23 & 7.36 (each d, J = 9 Hz, each 2 H, benzene-H_4), 10.71 (br, NH)

Reference Example 14

N-Methyl-N-[2-(3-pyridyl)ethyl]amine

(1) In 100 ml of $CHCl_3$ was dissolved 6.39 g (0.052 mole) of 2-(3-pyridyl)ethanol followed by dropwise addition of 15.6 ml of thionyl chloride with stirring at room temperature. Then, the mixture was stirred for 1.5 hours, after which the solvent was distilled off. After addition of ether, crystals were recovered by filtration and dried. The procedure gave 9.13 g of 2-(3-pyridyl)ethyl chloride hydrochloride as white crystals.

m.p.: 157-158 °C

NMR (DMSO-d_6) δ: 3.33 (t, J = 7 Hz, CH_2Cl), 4.02 (t, J = 7 Hz, CH_2-pyridine), 8.10 (dd, J = 6 & 8 Hz), 8.64 (m), 8.90 (d, J = 6 Hz), 9.00 (d, J = 2 Hz), 11.5 (br)

(2) To 32.6 g of 40% aqueous methylamine solution was added 7.48 g (0.042 mole) of 2-(3-pyridyl)ethyl chloride hydrochloride in small portions with stirring. The mixture was transfered to a stainless steel reaction column and heated at an external temperature of 80 °C for 4 hours. After cooling, 3.36 g of NaOH was added with ice-cooling and stirring and the mixture was saturated with sodium chloride and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and the CH_2Cl_2 was distilled off to give 6.32 g of the title compound in crude form as a yellow oil.

NMR ($CDCl_3$) δ: 1.58 (s, NH), 2.44 (s, NMe), 2.82 (m, CH_2CH_2), 7.21 (dd, J = 5 & 8 Hz, 1 H), 7.55 (m, 1 H), 8.47 (m, 2 H)

Reference Example 15

Pyridine-4-aldehyde and pyridine-2-aldehyde were respectively reacted with methylamine in the same manner as Reference Example 6 (1) to give the following compounds.

(1) N-(4-Pyridylmethylidene)methylamine (yellow oil)

NMR ($CDCl_3$) δ: 3.52 (d, J = 2 Hz, MeN), 7.53 (m, 2 H, pyridyl-H_2), 8.20 (m, CH = N), 8.65 (m, 2 H, pyridyl-H_2)

IR (neat): 1645, 1590, 1410, 995, 810 cm^{-1}

(2) N-(2-Pyridylmethylidene)methylamine (yellow oil)

NMR ($CDCl_3$) δ: 3.54 (d, J = 2 Hz, MeN), 7.30 (m, 1 H, pyridine-H_1), 7.71 (m, 1 H, pyridine-H_1), 7.97 (m, 1H, pyridine-H_1), 8.40 (m, CH = N), 8.31 (d, J = 5 Hz, 1 H, pyridine-H_1)

IR (neat): 1650, 1585, 1645, 1430, 990, 770 cm^{-1}

Reference Example 16

The compounds of Reference Example 15 (1) and (2) were respectively reacted in the same manner as Reference Example 6 (2) to give the following compounds.

(1) N-Methyl-N-(4-pyridylmethyl)amine (yellow brown oil)

NMR ($CDCl_3$) δ: 1.86 (br s, NH), 2.44 (s, Me), 3.76 (s, CH_2), 7.30 (m, 2 H, pyridine-H_2), 8.53 (m, 2 H, pyridine-H_2)

IR (neat): 3260, 1600, 1440, 1410, 790 cm^{-1}

(2) N-Methyl-N-(2-pyridylmethyl)amine (orange-colored oil)

NMR ($CDCl_3$) δ: 2.48 (s, Me), 3.87 (s, CH_2), 7.0-7.4 (m, 2 H, pyridine-H_2), 7.64 (t, J = 8 Hz, 1 H, pyridine-H_1), 8.56 (d, J = 4 Hz, pyridine-H_1)

IR (neat): 1590, 1570, 1470, 1430, 755 cm^{-1}

Reference Example 17

N-(6-Chloro-3-pyridylmethyl)-N-ethylamine

Using 6-chloro-3-pyridylmethyl chloride and 70% aqueous ethylamine solution, the reaction according to Reference Example 11 was carried out to give the title compound as a brown oil.

NMR ($CDCl_3$) δ: 1.11 (t, J = 7 Hz, CH_2CH_3), 1.43 (s, NH), 2.68 (q, J = 7 Hz, CH_2CH_3), 3.79 (s, CH_2-pyridine), 7.28 (d, J = 8 Hz, 1 H), 7.71 (dd, J = 2 & 8 Hz, 1 H), 8.33 (d, J = 2 Hz, 1 H)

IR (neat): 1595, 1565, 1460 (sh), 1450, 1380, 1100 cm^{-1}

Reference Example 18

O-Methyl-N-(3-pyridylmethyl)hydroxylamine

In 200 ml of acetonitrile was suspended 6.6 g (0.04 mole) of 3-pyridylmethyl chloride hydrochloride, followed by addition of 10 g (0.12 mole) of O-methylhydroxylamine hydrochloride and 16.2 g (0.16 mole) of triethylamine. The mixture was stirred at 50 °C for 15 hours. The insoluble matter was filtered off and the filtrate was concentrated. The residue was subjected to silica gel column chromatography, using EtOH-$CHCl_3$ (1:10) as an eluent. The procedure gave 1.0 g of the title compound as a yellow oil.

NMR ($CDCl_2$) δ: 3.47 (s, 3 H), 4.05 (s, 2 H), 5.73 (br, NH), 7.27 (dd, J = 8 & 5 Hz, 1 H), 7.73 (dt, J = 8 & 2 Hz, 1 H), 8.50-8.70 (m, 2 H)

IR (neat): 3200, 1580, 1425, 710 cm^{-1}

Reference Example 19

(2-Methoxy)ethyl isothiocyanate

In 70 ml of water was dissolved 4.6 g (0.11 mole) of NaOH. Then, 6.4 ml (0.11 mole) of carbon disulfide was added with vigorous stirring and 8.0 g (0.11 mole) of 2-methoxyethylamine was added gradually in droplets. The mixture was stirred at 70 °C for 2 hours, after which 8.2 ml (0.11 mole) of methyl chloroformate was added dropwise at room temperature. The mixture was stirred at 50 °C for 1 hour. The oil separated from the aqueous layer was extracted with ether and dried over $MgSO_4$. The ether was distilled off and the residue was distilled under reduced pressure to give 7.6 g of the title compound as a colorless oil.

b.p: 77-80 °C/22 mmHg

NMR ($CDCl_3$) δ: 3.41 (s, 3 H), 3.4-3.8 (m, 4 H)

IR (neat): 2080, 1720, 1340 cm^{-1}

Reference Example 20

6-Chloro-3-pyridylmethyl chloride and 6-chloro-3-pyridylmethyl chloride hydrochloride

(1) In 70 ml of MeOH was suspended 12.0 g (0.086 mole) of 6-hydroxynicotinic acid followed by addition of 4 ml of concentrated H_2SO_4. The mixtrue was refluxed for 10 hours. After cooling, MeOH was distilled off and the residue was adjusted to pH about 8 with a saturated aqueous solution of sodium hydrogen carbonate. The precipitate was collected by filtration, rinsed (twice) with water and dried to give 10.5 g of methyl 6-hydroxynicotinate as pale yellow crystals. This product was in the pyridone structure.

NMR (DMSO-d_6) δ: 3.77 (s, 3 H), 6.38 (d, J = 10 Hz, 1 H), 7.80 (dd, J = 10 & 3 Hz, 1 H), 8.05 (d, J = 3 Hz, 1 H), 11 (br)

(2) In 100 ml of acetonitrile was dissolved 4.0 g (0.026 mole) of methyl 6-hydroxynicotinate followed by addition of 0.9 ml of triethylamine. The mixture was refluxed and 3.7 ml of phosphorus oxychloride was added dropwise with stirring over a period of 15 minutes. The mixture was further refluxed for 3 hours. After cooling, the acetonitrile was distilled off and the residue was diluted with 20 ml of water and adjusted to pH about 8 with a saturated aqueous solution of sodium hydrogen carbonate. The resulting crystals are collected by filtration, rinsed with water and dried to give 3.6 g of methyl 6-chloronicotinate as pale yellow needles.

m.p.: 87-88 °C

MNR ($CDCl_3$) δ: 3.97 (s, 3 H), 7.44 (d, J = 8 Hz, 1 H), 8.27 (dd, J = 8 & 2 Hz, 1 H). 9.02 (d, J = 2 Hz, 1 H)

IR (Nujol): 1715, 1585, 1440, 1290, 1280, 1125 cm^{-1}

(3) To a mixture of 3.0 g (0.0175 mole) of methyl 6-chloronicotinate, 2.0 g of sodium borohydride and 60 ml of THF on reflux, 8.0 ml of MeOH was added with stirring over a period of 1 hour. After completion of the dropwise addition, the mixture was further refluxed for 30 minutes and when cold, the solvent was distilled off. The residue was diluted with 30 ml of water, saturated with NaCl and extracted with CH_2Cl_2 - (20 ml x 3). The CH_2Cl_2 layer was dried over $MgSO_4$ and the CH_2Cl_2 was distilled off to give 2.3 g of 6-chloro-3-pyridylmethanol as a yellow oil. When left standing at room temperature, this product was thoroughly crystallized.

NMR ($CDCl_3$) δ: 2.89 (br, 1 H), 4.69 (s, 2H), 7.28 (d, J = 9 Hz, 1 H), 7.69 (dd, J = 9 & 3 Hz, 1 H), 8.28 (d, J = 3 Hz, 1 H)

(4) In 500 ml of $CHCl_3$ was dissolved 47.3 g (0.33 mole) of 6-chloro-3-pyridylmethanol followed by dropwise addition of 99.3 ml of thionyl chloride with stirring at room temperature. After completion of the dropwise addition, the mixture was further stirred for 1.5 hours and, then, allowed to stand overnight. The $CHCl_3$ was distilled off under reduced pressure, whereby crystals and oil were obtained as a residue. The residue was diluted with ether, collected by filtration and dried to give 45.2 g of 6-chloro-3-pyridylmethyl chloride hydrochloride as white crystals.

NMR (DMSO-d_6) δ: 4.82 (s, 2 H), 7.51 (d, J = 8 Hz, 1 H), 7.97 (dd, J = 8 & 2 Hz, 1 H), 8.50 (d, J = 2 Hz, 1 H)

The mother liquor remaining after separation of the above crop of crystals was concentrated and the insoluble residue was dissolved in EtOH, diluted with toluene and concentrated. The above procedure was carried out for a total of 3 times to recover 9.04 g of crude 6-chloro-3-pyridylmethyl chloride as an oil.

(5) In 50 ml of water was suspended 15.0 g (0.076 mole) of 6-chloro-3-pyridylmethyl chloride hydrochloride and the suspension was adjusted to pH about 8 with a saturated aqueous solution of sodium hydrogen carbonate. The resulting mixture was extracted with ether (100 ml x 3) and dried over $MgSO_4$. The ether was then distilled off under reduced pressure to give a crystalline residue. After addition of hexane, the crystals were recovered by filtration, washed with hexane and dried to give 11.0 g of 6-chloro-3-pyridylmethyl chloride as white prisms.

m.p.: 39-40 °C

NMR ($CDCl_3$) δ: 4.56 (s, 2 H), 7.35 (d, J = 8 Hz, 1 H), 7.73 (dd, J = 8 & 2 Hz, 1 H), 8.40 (d, J = 2 Hz, 1 H)

IR (Nujol): 1585, 1445, 1280, 1135, 1105, 820, 740 cm^{-1}

Reference Example 21

N-Methyl-N-(2-pyrazinyl)methylamine

(1) In 300 ml of CCl_4 was dissolved 9.4 g (0.1 mole) of 2-methylpyrazine followed by addition of 13.4 g of N-chlorosuccinimide and 0.5 g of benzoyl peroxide. The mixture was refluxed for 24 hours. After cooling, the insoluble matter was filtered off and the filtrate was concentrated to give 11.0 g of 2-chloromethylpyrazine as oil.

NMR ($CDCl_3$) δ: 4.73 (s, 2 H), 8.36-8.70 (m, 2 H), 8.80 (s, 1 H)

(2) The reaction according to Reference Example 11 was carried out using 2-chloromethylpyrazine in lieu of 2,6-dichloro-3-pyridylmethyl chloride to give the title compound as oil.

NMR ($CDCl_3$) δ: 2.50 (s, 3 H), 2.63 (br, 1 H), 3.93 (s, 2 H), 8.45-8.60 (m, 2 H), 8.63 (s, 1 H)

Reference Example 22

1-[N-(6-Chloro-3-pyridylmethyl)-N-n-propyl]amino-1-methylthio-2-nitroethylene

(1) In 15 ml of acetonitrile was dissolved 6.05 g (0.0373 mole) of 6-chloro-3-pyridylmethyl chloride, and under cooling with ice-water and stirring, the solution was added dropwise to a solution of 10.97 g of n-propylamine in 50 ml of acetonitrile. After completion of the dropwise addition, the mixture was stirred at room temperature for 1 hour and at an external temperature of 50 °C for an additional 1 hour. The acetonitrile was distilled off and the residue was diluted with aqueous sodium hydrogen carbonate solution and extracted with CH_2Cl_2 (100 ml x 3). The extract was dried over $MgSO_4$ and distilled to remove CH_2Cl_2, whereby 6.94 g of N-(6-chloro-3-pyridylmethyl)-N-n-propylamine was obtained as a yellow-brown oil.

NMR ($CDCl_3$) δ: 0.90 (t, J = 7 Hz, CH_2CH_3), 1.32 (s, NH), 1.52 (sextet, J = 7 Hz, CH_2CH_3), 2.59 (t, J = 7 Hz, NCH_2CH_2), 3.79 (s, CH_2-pyridine), 7.29 (d, J = 8 Hz, 1 H), 7.71 (dd, J = 8 & 2 Hz, 1 H), 8.35 (d, J = 2 Hz, 1 H)

(2) In 100 ml of EtOH was dissolved 4.47 g of 1,1-bis(methylthio)-2-nitroethylene under heating at the reflux temperature. Then, with stirring and refluxing, a solution of 3.50 g (0.0190 mole) of N-(6-chloro-3-pyridylmethyl)-N-n-propylamine in 15 ml of EtOH was added dropwise and the mixture was further refluxed for 12.5 hours. The reaction mixture was allowed to stand at room temperature overnight and the resulting crystals were filtered off. The filtrate was concentrated and the residue was subjected to silica gel (250 g) column chromatography using EtOH-$CHCl_3$ (1:20) as an eluent. The procedure gave 2.98 g of the title compound as a yellow viscous oil.

NMR ($CDCl_3$) δ: 0.90 (t, J = 7 Hz, CH_2CH_3), 1.68 (sextet, J = 7 Hz, CH_2CH_3), 2.46 (s, MeS), 3.42 (t, J = 7 Hz, NCH_2CH_2), 4.70 (s, CH_2-pyridine), 6.80 (s, $=CHNO_2$), 7.36 (d, J = 8 Hz, 1 H), 7.61 (dd, J = 8 & 2 Hz, 1 H), 8.29 (d, J = 2 Hz, 1 H)

Reference Example 23

1-[N-(6-Chloro-3-pyridylmethyl)-N-i-propyl]amino-1-methylthio-2-nitroethylene

The reactions according to (1) and (2) of Reference Example 22 were carried out using i-propylamine in lieu of n-propylamine to give the following compounds at the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N-i-propylamine (oil)

NMR ($CDCl_3$) δ: 1.07 (d, J = 6 Hz, Me_2CH), 1.21 (br s, NH), 2.84 (septet, J = 6 Hz, $CHMe_2$), 3.77 (s, CH_2), 7.28 (d, J = 8 Hz, 1 H), 7.71 (dd, J = 8 & 2 Hz, 1 H), 8.35 (d, J = 2 Hz, 1 H)

(2) Title compound (viscous oil)

NMR ($CDCl_3$) δ: 1.35 (d, J = 7 Hz, $CHMe_2$), 2.38 (s, MeS), 4.64 (s, CH_2), 6.57 (s, $=CHNO_2$)

Reference Example 24

2-Chloro-5-methylaminopyridine

To 5.0 g (0.039 mole) of 5-amino-2-chloropyridine was added 40 ml of ethyl orthoformate and the mixture was refluxed for 5 hours. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in 50 ml of EtOH. After addition of 1.8 g of sodium borohydride, the mixture was

stirred at 70-80 °C for 3 hours. The reaction mixture was concentrated and after addition of 50 ml of iced water and 5 ml of concentrated hydrochloric acid, the mixture was adjusted to pH 7-8 with $NaHCO_3$ and extracted with AcOEt (50 ml x 3). The AcOEt layers were pooled, washed with water and dried over $MgSO_4$. The AcOEt was distilled off and hexane was added to the crystalline residue. The crystals are collected by filtration, washed with hexane and dried to give 5.1 g of the title compound as white crystals.

m.p.: 70 °C

NMR ($CDCl_3$) δ: 2.85 (br d, J = 4.5 Hz, 3 H), 3.3-4.3 (m, 1 H), 6.87 (dd, J = 8.0 & 3.0 Hz, 1 H), 7.11 (d, J = 8.7 Hz, 1 H), 7.78 (d, J = 3.3 Hz, 1 H)

Reference Example 25

N-(2,6-Dimethyl-4-pyridylmethyl)-N-methylamine

(1) In 77 ml of $CHCl_3$ was dissolved 7.00 g (0.0511 mole) of (2,6-dimethyl-4-pyridyl)methanol and with stirring at room temperature, 15.3 ml of thionyl chloride was added dropwise. After completion of the dropwise addition, the mixture was stirred for 3 hours and concentrated. The residue was diluted with aqueous sodium hydrogen carbonate solution and extracted with AcOEt (100 ml x 3). The extract was dried over $MgSO_4$ and distilled to remove AcOEt. The procedure gave 6.37 g of (2,6-dimethyl-4-pyridyl)-methyl chloride as oil.

NMR ($CDCl_3$) δ: 2.53 (s, Me x 2), 4.45 (s, CH_2), 6.98 (s, pyridine-H_2)

(2) The reaction according to Reference Example 11 was carried out using (2,6-dimethyl-4-pyridyl)methyl chloride in lieu of 2,6-dichloro-3-pyridylmethyl chloride to give the title compound as oil.

NMR ($CDCl_3$) : 2.44 (s, NMe), 2.50 (s, pyridine-Me x 2), 3.68 (s, CH_2), 6.94 (s, pyridine-H_2)

Reference Example 26

N-(2-Chloro-3-pyridylmethyl)-N-methylamine

(1) To 10.24g(0.065 mole) of 2-chloronicotinic acid were added 20 ml of 1,2-dichloroethane and 9.5 ml of thionyl chloride and the mixture was refluxed for 1 hour. The reaction mixture was concentrated to give 11.9 g of 2-chloronicotinyl chloride as an orange-colored oil. When left standing at room temperature, this product solidified thoroughly.

NMR ($CDCl_3$) δ: 7.54 (dd, J = 8 & 5 Hz, 1 H), 8.48 (dd, J = 8 & 1 Hz, 1 H), 8.65 (dd, J = 5 & 1 Hz, 1 H)

(2) In 100 ml of cold water was dissolved 8.98 g of sodium borohydride and with ice-cooling and stirring, 11.7 g (0.0665 mole) of 2-chloronicotinyl chloride was added in small portions. The mixture was further stirred at the same temperature for 30 minutes and, then, extracted with Et_2O (100 ml x 3). The extract was dried over $MgSO_4$ and distilled to remove Et_2O. The procedure gave 8.75 g of (2-chloro-3-pyridyl)-methanol as a pale yellow oil. When left standing at room temperature, this product solidified thoroughly.

NMR ($CDCl_3$) δ: 4.53 (br, OH), 4.77 (s, CH_2), 7.30 (m, 1 H), 7.97 (m, 1 H), 8.25 (m, 1 H)

(3) The reaction according to Reference Example 25 (1) was carried out using (2-chloro-3-pyridyl)-methanol in lieu of (2,6-dimethyl-4-pyridyl)methanol to give (2-chloro-3-pyridyl)methyl chloride as a yellow oil.

NMR ($CDCl_3$) δ: 4.71 (s, CH_2), 7.31 (dd, J = 8 & 5 Hz, 1 H), 7.88 (dd, J = 8 & 2 Hz, 1 H), 8.33 (dd, J = 5 & 2 Hz, 1 H)

(4) The reaction according to Reference Example 11 was carried out using (2-chloro-3-pyridyl)methyl chloride in lieu of 2,6-dichloro-3-pyridylmethyl chloride to give the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 1.95 (s, NH), 2.47 (s, Me), 3.84 (s, CH_2), 7.26 (dd, J = 8 & 5 Hz, 1 H), 7.80 (dd, J = 8 & 2 Hz, 1 H), 8.30 (dd, J = 5 & 2 Hz, 1 H)

Reference Example 27

2-Methyl-5-methylaminopyridine oxalate

To 5.0 g (0.04 mole) of 5-amino-2-methylpyridine was added 40 ml of ethyl orthoformate and the mixture was refluxed for 1 hour. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in 50 ml of EtOH, followed by addition of 2.1 g of sodium borohydride. The mixture was refluxed with stirring for 2.5 hours. The reaction mixture was concentrated and 50 ml of ice-water and 8

ml of concentrated hydrochloric acid were added to the residue. The mixture was adjusted to pH 7 with $NaHCO_3$ and extracted with AcOET (50 ml, 30 ml x 2). The AcOET layers were combined, washed with aqueous sodium chloride solution and dried over $MgSO_4$. The AcOEt was distilled off and the residue was diluted with Et_2O and the insoluble matter was filtered off. To the filtrate was added a solution of oxalic acid in EtOH (ca. 10%) and the resulting crystals were collected by filtration, washed with EtOH and dried. The procedure gave 4.3 g of the title compound as pale yellow crystals.

m.p.: 118.5-119.5 °C

NMR (DMSO-d_6) δ: 2.43 (3 H, s), 2.73 (3 H, s), 7.1-7.5 (2 H, m), 7.8-8.0 (1 H, m), 8.2-9.0 (m)

Reference Example 28

N-(5-Bromo-3-pyridylmethyl)-N-methylamine

The steps (1), (2), (3) and (4) of Reference Example 26 were repeated except that 5-bromonicotinic acid was used in lieu of 2-chloronicotinic acid to obtain the following compounds in the respective steps.

(1) 5-Bromonicotinyl chloride (white crystals)

NMR ($CDCl_3$) δ: 8.54 (m, 1 H), 8.99 (d, J = 1 Hz, 1 H), 9.25 (d, J = 1 Hz, 1 H)

(2) (5-Bromo-3-pyridyl)methanol (crude orange-colored oil)

NMR ($CDCl_3$) δ: 4.39 (br s, OH), 4.73 (s, CH_2), 7.90 (m, 1 H), 8.47 (d, J = 1 Hz, 1 H), 8.55 (d, J = 2 Hz, 1 H)

(3) (5-Bromo-3-pyridyl)methyl chloride (crude oil)

NMR ($CDCl_3$) δ: 4.57 (s, CH_2), 7.92 (m, 1 H), 8.56 (d, J = 1 Hz, 1 H), 8.65 (d, J = 1 Hz, 1 H)

(4) Title compound (crude oil)

NMR ($CDCl_3$) δ: 2.44 (s, Me), 3.76 (s, CH_2), 7.89 (m, 1 H), 8.48 (d, J = 1 Hz, 1 H), 8.57 (d, J = 1 Hz, 1 H)

Reference Example 29

N-(2-Methylthio-3-pyridylmethyl)-N-methylamine

The steps (1), (2), (3) and (4) of Reference Example 26 were repeated except that 2-methylthionicotinic acid was used in lieu of 2-chloronicotinic acid to obtain the following compounds in the respective steps.

(1) 2-Methylthionicotinyl chloride (white - pale yellow crystals)

NMR ($CDCl_3$) δ: 2.56 (s, MeS), 7.17 (dd, J = 5 & 8 Hz, 1 H), 8.52 (dd, J = 8 & 2 Hz, 1 H), 8.67 (dd, J = 5 & 2 Hz, 1 H)

(2) (2-Methylthio-3-pyridyl)methanol (pale yellow oil, crystallized thoroughly on standing)

NMR ($CDCl_3$) δ: 2.56 (s, MeS), 3.46 (br s, OH), 4.62 (s, CH_2), 6.99 (dd, J = 5 & 8 Hz, 1 H), 7.62 (dd, J = 8 & 1 Hz, 1 H), 8.33 (dd, J = 5 & 8 Hz, 1 H)

(3) (2-Methylthio-3-pyridyl)methyl chloride (pale yellow oil)

NMR ($CDCl_3$) δ: 2.61 (s, MeS), 4.60 (s, CH_2), 6.99 (dd, J = 5 & 8 Hz, 1 H), 7.58 (dd, J = 8 & 2 Hz, 1 H), 8.43 (dd, J = 5 & 2 Hz, 1 H)

(4) Title compound (yellow oil)

NMR ($CDCl_3$) δ: 1.50 (s, NH), 2.44 (s, MeN), 2.57 (s, MeS), 3.73 (s, CH_2), 6.97 (dd, J = 5 & 8 Hz, 1 H), 7.51 (dd, J = 8 & 1 Hz, 1 H), 8.37 (dd, J = 5 & 1 Hz, 1 H)

Reference Example 30

N-Methyl-N-(4-thiazolyl)methylamine

(1) The reaction procedure of Reference Example 21 (1) was repeated except that 4-methylthiazole was used in lieu of 2-methylpyrazine to give crude 4-chloromethylthiazole as oil.

NMR ($CDCl_3$) δ: 4.72 (s, CH_2Cl), 7.37 (m, 1 H), 8.78 (d, J = 2 Hz, 1 H)

(2) The reaction procedure of Reference Example 11 was repeated except that crude 4-chloromethylthiazole was used in lieu of 2,6-dichloro-3-pyridylmethyl chloride and the reaction was conducted at room temperature for 1 hour and further at 50 °C for 2 hours. The procedure gave the title compound as a crude oil.

NMR ($CDCl_3$) δ: 2.43 (s, MeN), 3.89 (s, CH_2), 7.17 (m, 1 H), 8.74 (d, J = 2 Hz, 1 H)

Reference Example 31

2-Chloro-5-ethylaminopyridine

A mixture of 10 g (0.078 mole) of 5-amino-2-chloropyridine and 50 ml of ethyl orthoacetate was refluxed for 2 hours. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in 60 ml of dry THF. Then, the solution was added dropwise to a suspension of 7.0 g of lithium borohydride in 100 ml of dry THF over a period of 15 minutes with constant stirring. After completion of dropwise addition, the mixture was refluxed with stirring for 27 hours. After cooling, the solvent was distilled off. To the residue were added 100 ml of ice-water and 35 ml of concentrated hydrochloric acid and the mixture was heated at 67 °C for a while. After cooling, the reaction mixture was adjusted to pH 7 with $NaHCO_3$ and extracted with AcOEt (50 ml x 3). The AcOEt layers were combined, washed with aqueous sodium chloride solution and dried over $MgSO_4$. The AcOEt was distilled off and the residual crystals were collected by filtration, washed with hexane and dried. The procedure gave 9.2 g of the title compound as pale yellowish green crystals.

m.p.: 65-66 °C

NMR ($CDCl_3$) δ: 1.25 (3 H, t, J = 7.4 Hz), 2.9-3.4 (2 H, m), 3.4-4.1 (1 H, m, NH), 6.86 (1 H, dd, J = 9.0 & 3.0 Hz), 7.09 (1 H, d, J = 7.8 Hz), 7.77 (1 H, d, J = 2.7 Hz)

Reference Example 32

2-Chloro-5-n-propylaminopyridine

(1) To 6.4 g (0.05 mole) of 5-amino-2-chloropyridine was added 25 g of triethyl orthopropionate and the mixture was refluxed for 3 hours. Then, at an external temperature of 70 °C, the reaction mixture was concentrated under reduced pressure using a vacuum pump. The procedure gave 10.5 g of N-(6-chloro-3-pyridyl)-O-ethylpropionimidate as a yellow oil.

NMR ($CDCl_3$) δ: 1.07 (t, J = 8 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 2.16 (q, J = 8 Hz, 2 H), 4.22 (q, J = 7 Hz, 2 H), 7.06 (dd, J = 8 & 3 Hz, 1 H), 7.25 (d, J = 8 Hz, 1 H), 7.87 (d, J = 3 Hz, 1 H)

(2) To a 70% solution of sodium dihydro-bis(2-methoxyethoxy)aluminate in toluene was added 100 ml of toluene and a solution of 8.5 g (0.04 mole) of N-(6-chloro-3-pyridyl)-O-ethylpropionimidate in 20 ml of toluene was added dropwise over 5 minutes with stirring at room temperature. The mixture was further stirred at room temperature for 1 hour and at 50 °C for 2 hours, after which 50 ml of water was added dropwise over 5 minutes under ice-cooling. The mixture was stirred at 50 °C for 15 minutes. The toluene layer was separated, dried over $MgSO_4$ and concentrated and the residue was subjected to silica gel column chromatography using hexane-acetone (2:1) as the eluent. The procedure gave 5.9 g of the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 0.99 (t, J = 7 Hz, 3 H), 1.65 (m, 2 H), 3.07 (dt, J = 7 & 6 Hz, 2 H), 3.83 (br, 1 H), 6.86 (dd, J = 8 & 3 Hz, 1 H), 7.10 (d, J = 8 Hz, 1 H), 7.77 (d, J = 3 Hz, 1 H)

Reference Example 33

2-Chloro-5-n-butylaminopyridine

The steps (1) and (2) of Reference Example 32 were repeated except that trimethyl orthobutyrate was used in lieu of triethyl orthopropionate to obtain the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridyl)-O-methyl butyrimidate (yellow oil)

NMR ($CDCl_3$) δ: 0.85 (t, J = 7 Hz, 3 H), 1.33-1.80 (m, 2 H), 2.16 (t, J = 7 Hz, 2 H), 3.80 (s, 3 H), 7.06 (dd, J = 8 & 3 Hz, 1 H), 7.27 (d, J = 8 Hz, 1 H), 7.88 (d, J = 3 Hz, 1 H)

(2) Title compound (yellow crystals)

m.p.: 46-48 °C

NMR ($CDCl_3$) δ: 0.93 (t, J = 7 Hz, 3 H), 1.16-1.83 (m, 4 H), 3.08 (dt, J = 7 & 6 Hz, 2 H), 3.78 (br, 1 H), 6.84 (dd, J = 8 & 3 Hz, 1 H), 7.08 (d, J = 8 Hz, 1 H), 7.75 (d, J = 3 Hz, 1 H)

Reference Example 34

3-Methylamino-5-trifluoromethylpyridine

The reaction procedure of Reference Example 24 was repeated except that 3-amino-5-trifluoromethylpyridine was used in lieu of 5-amino-2-chloropyridine to obtain the title compound as white crystals.

m.p.: 69-70 °C

NMR (CDC_3): 2.89 (3 H, d, J = 5.1 Hz), 3.8-4.5 (1 H, m, NH), 6.9-7.1 (1 H, m), 8.1-8.3 (2 H, m)

Reference Example 35

N-Methyl-N-(6-methyl-3-pyridylmethyl)amine

(1) The reaction procedure of Reference Example 20 (3) was repeated except that methyl 6-methylnicotinate was used in lieu of methyl 6-chloronicotinate to give crude 6-methyl-3-pyridylmethanol as a yellow oil.

NMR ($CDCl_3$) δ: 2.49 (s, Me), 4.66 (s, CH_2), 4.93 (br, OH), 7.14 (d, J = 8 Hz, 1 H), 7.63 (dd, J = 8 & 2 Hz, 1 H), 8.36 (d, J = 2 Hz, 1 H)

(2) The reaction procedure of Reference Example 25 (1) was repeated except that crude 6-methyl-3-pyridylmethanol was used in lieu of (2,6-dimethyl-4-pyridyl)methanol to give crude (6-methyl-3-pyridyl)-methyl chloride as oil.

NMR ($CDCl_3$) δ: 2.54 (s, Me), 4.55 (s, CH_2), 7.16 (d, J = 8 Hz, 1 H), 7.62 (dd, J = 8 & 2 Hz, 1 H), 8.49 (dd, J = 2 Hz, 1 H)

(3) A mixture of 16.6 g of 40% aqueous $MeNH_2$ solution and 52 ml of CH_3CN was cooled with ice and 6.08 g (0.043 mole in terms of pure product) of crude (6-methyl-3-pyridyl)methyl chloride was added dropwise with constant stirring. After completion of dropwise addition, the mixture was stirred at room temperature for 1.5 hours, at the end of which time the solvent was distilled off. The solid residue was extracted with CH_2Cl_2 and the CH_2Cl_2 layer was dried over $MgSO_4$. The CH_2Cl_2 was distilled off and the residue was diluted with 70 ml of Et_2O and filtered to remove the insoluble matter. Finally the filtrate was concentrated to recover 4.60 g of the title compound as a crude oil.

NMR ($CDCl_3$) δ: 2.43 (s, MeN), 2.53 (s, pyridine-Me), 3.71 (s, CH_2), 7.13 (d, J = 8 Hz, 1 H), 7.57 (dd, J = 8 & 2 Hz, 1 H), 8.40 (d, J = 2 Hz, 1 H)

Reference Example 36

N-(6-Fluoro-3-pyridylmethyl)-N-methylamine

(1) A mixture of 7.2 g (0.0648 mole) of 2-fluoro-5-methylpyridine, 12.0 g of N-bromosuccinimide, 0.5 g of benzoyl peroxide and 200 ml of CCl_4 was refluxed for 2 hours. After cooling, the precipitate was filtered off and the filtrate was washed with water and dried. Finally, the CCl_4 was distilled off to recover 12.68 g of crude (6-fluoro-3-pyridyl)methyl bromide as a pale yellow oil.

NMR ($CDCl_3$) δ: 4.47 (2 H, s, CH_2), 6.96 (1 H, dd, J = 8.4 & 2.7 Hz), 7.56 (1 H, ddd, J = 8.4, 2.4 & 8.4 Hz), 8.29 (1 H, d, J = 2.4 Hz)

(2) To a mixture of 2.5 g of 40% aqueous methylamine solution and 30 ml of CH_3CN was added dropwise 3.0 g of crude (6-fluoro-3-pyridyl)methyl bromide with constant stirring. The mixture was allowed to stand at room temperature overnight and concentrated under reduced pressure. The residue was extracted with AcOEt and the extract was dried over $MgSO_4$ and concentrated. The procedure gave 1.35 g of the title compound as a crude orange-colored oil.

NMR ($CDCl_3$) δ: 2.53 (3 H, s, Me), 3.94 (2 H, s, CH_2) 5.40 (1 H, s, NH)

Reference Example 37

N-(6-Bromo-3-pyridylmethyl)-N-methylamine

(1) The reaction procedure of Reference Example 36 (1) was repeated except that 2-bromo-5-methylpyridine was used in lieu of 2-fluoro-5-methylpyridine to recover crude (6-bromo-3-pyridyl)methyl bromide as a yellow oil.

NMR ($CDCl_3$) δ: 4.42 (2 H, s), 7.48 (1 H, d, J = 8.4 Hz), 7.61 (1 H, dd, J = 8.4 & 2.7 Hz), 8.40 (1 H, d,

J = 2.7 Hz)

(2) To a mixture of 12.3 g of 40% aqueous methylamine solution and 40 ml of CH_3CN was added 8.0 g of crude (6-bromo-3-pyridyl)methyl bromide with stirring. The mixture was further stirred at room temperature for 30 minutes. The reaction mixture thus obtained was concentrated and the residue was diluted with toluene and subjected to azeotropic distillation to remove the water. Then, the soluble fraction was extracted with Et_2O. The Et_2O layer was dried over $MgSO_4$ and concentrated to recover 4.4 g of the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 2.48 (3 H, s), 2.73 (1 H, s), 3.80 (2 H, s), 7.45 (1 H, d, J = 8.4 Hz), 7.63 (1 H, dd, J = 8.4 & 2.7 Hz), 8.36 (1 H, d, J = 2.7 Hz)

Reference Example 38

N-(6-Bromo-3-pyridylmethyl)-N-ethylamine

The reaction procedure of Reference Example 37 (2) was repeated except that 70% aqueous ethylamine solution was used in lieu of 40% aqueous methylamine solution to recover the title compound as a crude oil.

NMR ($CDCl_3$) δ: 1.11 (3 H, t, J = 8.1 Hz), 2.16 (1 H, br s), 2.68 (2 H, q, J = 8.1 Hz), 3.78 (2 H, s), 7.45 (1 H, d, J = 8.4 Hz), 7.58 (1 H, dd, J = 8.4 & 2.7 Hz), 8.33 (1 H, d, J = 2.7 Hz)

Reference Example 39

N-(2-Chloro-5-thiazolylmethyl)-N-methylamine

The reaction procedure of Reference Example 11 was repeated except that crude 2-chloro-5-chloromethylthiazole was used in lieu of 2,6-dichloro-3-pyridylmethyl chloride and that CH_2Cl_2 was used as the extractant. The procedure gave the title compound as a crude oil.

NMR ($CDCl_3$) δ: 2.45 (s, MeN), 3.89 (s, CH_2), 7.37 (s, thiazole-H)

Reference Example 40

N-(2-Chloro-5-thiazolylmethyl)-N-ethylamine

The reaction procedure of Reference Example 17 was repeated except that crude 2-chloro-5-chloromethylthiazole was used in lieu of 6-chloro-3-pyridylmethyl chloride and that CH_2Cl_2 was used as the extractant. The procedure gave the title compound as a crude oil.

NMR ($CDCl_3$) δ: 1.10 (t, J = 7 Hz, $CH_2\underline{CH_3}$), 2.69 (q, J = 7 Hz, $\underline{CH_2}CH_3$), 3.93 (s, CH_2N), 7.36 (s, thiazole-H)

Reference Example 41

2-Chloro-5-thiazolylmethylamine

(1) The reaction procedure of Reference Example 10 (1) was repeated except that crude 2-chloro-5-chloromethylthiazole was used in lieu of 2,6-dichloro-3-pyridylmethyl chloride to give N-(2-chloro-5-thiazolylmethyl)phthalimide as pale yellow crystals.

m.p.: 108-109 °C

NMR ($CDCl_3$) δ: 4.97 (2 H, s), 7.60 (1 H, s), 7.6-8.1 (m, 4 H)

(2) The reaction procedure of Reference Example 3 was repeated except that N-(2-chloro-5-thiazolylmethyl)phthalimide was used in lieu of N-(6-chloro-3-pyridylmethyl)phthalimide to give the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 1.68 (2 H, br s), 4.04 (2 H, s), 7.38 (1 H, s)

Reference Example 42

2-Methoxy-5-methylaminopyridine

The reaction procedure of Reference Example 24 was repeated except that 5-amino-2-methoxypyridine was used in lieu of 5-amino-2-chloropyridine to give the title compound as a yellow oil.

NMR ($CDCl_3$) δ: 2.81 (3 H, s), 3.1-3.8 (1 H, m), 3.87 (3 H, s), 6.64 (1 H, d, J = 9.0 Hz), 6.98 (1 H, dd, J = 8.7 & 3.2 Hz), 7.59 (1 H, d, J = 2.4 Hz)

Reference Example 43

6-Bromo-3-pyridylmethylamine

(1) The reaction procedure of Reference Example 10 (1) was repeated except that crude 6-bromo-3-pyridylmethyl bromide was used in lieu of 2,6-dichloro-3-pyridylmethyl chloride, to give N-(6-bromo-3-pyridylmethyl)phthalimide as white crystals.

m.p.: 130-131 °C

NMR ($CDCl_3$)δ: 4.83(s,2H), 7.44 (d,J = 8Hz,1H), 7.6-8.0 (m,5H), 8.49 (d,J = 2Hz,1H)

(2) The reaction procedure of Reference Example 3 was repeated except that N-(6-bromo-3-pyridylmethyl)phthalimide was used in lieu of N-(6-chloro-3-pyridylmethyl)phthalimide, to give the title compound as pale yellow crystals.

m.p.: 57-58 °C

NMR ($CDCl_3$)δ: 1.46 (br s,2H), 3.86 (s,2H), 7.42 (d, J = 8Hz,1H), 7.58 (dd,J = 8&2Hz,1H), 8.32 (d,J = 2Hz,1H)

Reference Example 44

N-(6-Chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)amine

In 15 ml of water was dissolved 12.55 g of 2,2,2-trifluoroethylamine hydrochloride, followed by addition of 68 ml of CH_3CN, and further 9.35 g of Et_3N and then 3.00 g (0.0185 mole) of 6-chloro-3-pyridylmethyl chloride under cooling with ice-water and stirring. The mixture was stirred at room temperature for one hour, at 50 °C for one hour and at 70 °C for 90 hours. The CH_3CN was distilled off, and the residue was followed by addition of $NaHCO_3$ and then extracted with CH_2Cl_2 (100 ml x 3). The extract was dried over $MgSO_4$ and distilled to remove CH_2Cl_2. To the residue was added 100 ml of Et_2O and the resulting unsoluble matter was filtered off. The filtrate was concentrated to give 3.85 g of the title compound as yellow oil.

NMR ($CDCl_3$)δ: 1.81 (br,NH), 3.21 (q,J = 9Hz,CF_3CH_2), 3.92 (s,pyridine-CH_2), 7.30 (d,J = 8Hz,1H), 7.71 (dd, J = 8&2Hz,1H), 8.32 (d,J = 2Hz,1H)

Example 1

1-Methylthio-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 1-1) and 1,1-bis(3-pyridylmethyl)amino-2-nitroethylene (Compound 1-2)

In 100 ml of EtOH was dissolved 5.0 g (0.03 mole) of 1,1-bis(methylthio)-2-nitroethylene with heating and, then, a solution of 3.2 g (0.03 mole) of 3-pyridylmethylamine in 30 ml of EtOH was added dropwise in 3 installments at intervals of 20-30 minutes while refluxing. The mixture was further refluxed for 2 hours and the EtOH was distilled off. The residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (5:1) as an eluent. The procedure gave 4.0 g and 0.5 g of the title Compounds (1-1 and 1-2), respectively, each as a white powder.

Compound 1-1

m.p.: 129-130 °C

Compound 1-2

m.p.: 141-143 °C
NMR (DMSO-d_6) δ: 4.55 (d), 6.52 (s), 10.26 (br s)
IR (Nujol): 3150, 1575, 1390 cm^{-1}

Example 2

1-Methylthio-1-(N-methyl-N-3-pyridylmethyl)amino-2-nitroethylene (Compound 2)

The procedure of Example 1 was repeated except that N-methyl-N-pyridylmethylamine was used in lieu of 3-pyridylmethylamine to give the title compound as a pale yellow viscous oil.
NMR ($CDCl_3$) δ: 2.50 (s), 3.06 (s), 4.81 (s), 6.81 (s)

Example 3

1-Methylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 3)

In 50 ml of EtOH was dissolved 2.3 g (0.01 mole) of 1-methylthio-1-(3-pyridylmethyl)amino-2-nitroethylene with heating and, then, a solution of 1.2 g (0.015 mole) of 40% aqueous methylamine in 10 ml of EtOH was added dropwise over a period of 30 minutes while refluxing. The mixture was further refluxed for 2 hours, after which it was concentrated. The crystals were collected by filtration and recrystallized from acetonitrile to give 1.6 g of the title compound as white prisms.
m.p.:159-160 °C
NMR (DMSO-d_6) δ: 2.86 (br s), 4.49 (d), 6.46 (s)

Example 4

1-Methylthio-1-(3-pyridylmethyl)amino-2-nitroethylene was reacted with various amines (or ammonium) in the same manner as Example 3 and the reaction product was purified by recrystallization or silica gel column chromatography to give the following compounds 4 - 22.

(1) 1-Ethylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 4)
m.p.: 161-162 °C

(2) 1-iso-Propylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 5)
m.p.: 148-150 °C
NMR ($CDCl_3$) δ: 4.46 (d), 6.52 (s), 7.28 (br s), 10.1 (br s)

(3) 1-n-Butylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 6)
m.p.: 110-112 °C

(4) 1-Allylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 7)
m.p.: 114-115 °C

(5) 1-n-Pentylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 8)
m.p.: 97-98 °C

(6) 1-Anilino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 9)
m.p.: 217-218 °C

(7) 1-Amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 10)
m.p.: 177-178 °C (decompn.)

(8) 1-(2-n-Propylthioethyl)amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 11) (white prisms)
m.p.: 93-94 °C
NMR ($CDCl_3$) δ: 4.48 (d), 6.23 (br s), 6.63 (s), 10.5 (br s)

(9) 1-(2-Dimethylaminoethyl)amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 12)(white prisms)
m.p.: 110-111 °C
NMR ($CDCl_3$) δ: 2.02 (s), 4.30 (m), 6.60 (s), 10.3 (br s)

(10) 1-(2-Hydroxyethyl)amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 13)
m.p. 161-163 °C

(11) 1-(2-Methoxyethyl)amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 14)
m.p.: 108-109 °C

(12) 1-(2,2-Dimethoxyethyl)amino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 15) (white prisms)
m.p.: 96-98 °C
NMR ($CDCl_3$) δ: 6.55 (s), 6.85 (br s), 10.3 (br s)
(13) 1-(3-Pyridylmethyl)amino-1-(2,2,2-trifluoroethyl)amino-2-nitroethylene (Compound 16)
m.p.: 164-165 °C
NMR (DMSO-d_6) δ: 4.09 (m), 6.58 (s)
(14) 1-(3-Pyridylmethyl)amino-1-(trimethylsilylmethyl)amino-2-nitroethylene (Compound 17)
m.p.: 156-157 °C
NMR ($CDCl_3$) δ: 0.10 (s), 2.67 (d), 4.32 (d), 6.37 (s), 7.12 (br s), 10.1 (br s)
(15) 1-Hydrazino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 18)
m.p.: 176-177 °C (decompn.)
(16) 1-Dimethylamino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 19)
m.p.: 68-70 °C
NMR ($CDCl_3$) δ: 2.93 (s), 4.48 (d), 6.52 (s), 9.77 (br s)
(17) 1-(3-Pyridylmethyl)amino-1-pyrrolidino-2-nitroethylene (Compound 20) (pale yellow powder)
m.p.: 103-105 °C
NMR ($CDCl_3$) δ: 4.61 (d), 6.63 (s), 10.42 (br s)
(18) 1-(4-Methylpiperazino)-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 21)
NMR ($CDCl_3$) δ: 2.32 (s), 2.46 (t), 3.25 (t), 4.53 (d), 6.50 (s), 9.73 (br s)
(19) 1-(Morpholino)-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 22)
m.p.: 102-103 °C

Example 5

1-Piperidino-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 23)

In 20 ml of EtOH was dissolved 0.8 g (0.004 mole) of 1-methylthio-1-piperidino-2-nitroethylene followed by addition of 0.4 g (0.004 mole) of 3-pyridiylmethylamine. The mixture was refluxed for 2 hours. The ethanol was distilled off and the residue was purified by silica gel column chromatography to give 0.3 g of the title compound as a pale yellow powder.
m.p.: 106-108 °C

Example 6

1-(2,2-Dimethyl-1-hydrazino)-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 24)

The procedure of Example 5 was repeated using 1-(2,2-dimethyl-1-hydrazino)-1-methylthio-2-nitroethylene to give the title compound as white prisms.
m.p.: 158-159 °C
NMR ($CDCl_3$) δ: 2.63 (s), 4.36 (d), 6.45 (s), 6.85 (br s), 10.36 (br s)

Example 7

1-Amino-1-(N-methyl-N-3-pyridylmethyl)amino-2-nitroethylene (Compound 25)

In 50 ml of MeOH was dissolved 7.2 g (0.03 mole) of 1-methylthio-1-(N-methyl-N-3-pyridylmethyl)-amino-2-nitroethylene followed by addition of 10 ml of 25% aqueous ammonia. The mixture was refluxed for 2 hours, after which the solvent was distilled off. The residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (5:1) as an eluent to give 1.5 g of the title compound as white prisms.
m.p.:158-159 °C
NMR (DMSO-d_6) δ: 3.06 (s), 4.66 (s), 6.63 (s), 8.93 (br s)

Example 8

1-Methylamino-1-(N-methyl-N-3-pyridylmethyl)amino-2-nitroethylene (Compound 26)

(1) In 30 ml of toluene was dissolved 2.5 g (0.02 mole) of N-methyl-N-3-pyridylmethylamine followed by addition of 1.5 g (0.02 mole) of methyl isothiocyanate and the mixture was stirred at room temperature overnight. Finally, the solvent was distilled off to give 3.8 g of N-methyl-N'-methyl-N'-3-pyridylmethylthiourea as a yellow viscous oil. This oily product was purified by silica gel column chromatography using HeOH-$CHCl_3$ (1:10) as an eluent to give crystals.

m.p. : 86-87 °C

NMR ($CDCl_3$) δ: 3.06 (s), 3.17 (d), 5.22 (s), 6.16 (br s), 7.28 (dd. J = 8 & 5 Hz, 1H), 7.74 (m. 1H), 8.54 (m. 2H)

(2) In 30 ml of MeOH was dissolved 3.8 g (0.02 mole) of the N-methyl-N'-methyl-N'-3-pyridylmethylthiourea obtained in (1) followed by addition of 2.8 g (0.02 mole) of methyl iodide. The mixture was refluxed for 4 hours. The solvent was distilled off and the residue was diluted with 10 ml of a saturated aqueous solution of sodium hydrogen carbonate and extracted with AcOEt (50 ml x 3). The extract was dried over $MgSO_4$ and the solvent was distilled off to give 1.0 g of crude S-methyl-N-methyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea as a yellow oil.

NMR ($CDCl_3$) δ: 2.33 (s), 2.83 (s), 3.26 (s), 4.56 (s), 7.25(dd, J = 8 & 5 Hz, 1H), 7.60(m, 1H), 8.55(m, 2H)

(3) To 1.0 g (0.048 mole) of the S-methyl-N-methyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea obtained in (2) was added 5 ml of nitromethane and the mixture was stirred at 90 °C for 15 hours. The nitromethane was distilled off and the residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (5:1) as an eluent to give 0.3 g of the title compound as a yellow viscous oil. This product was cooled (to 5 °C) and the resulting crystals were washed with ethyl acetate and dried. The melting point of this product was 86-87 °C.

NMR ($CDCl_3$) δ: 2.83 (s), 3.07 (d), 4.43 (s), 6.53 (s), 7.35 (dd, J = 8 & 5 Hz, 1H), 7.61(m, 1H), 8.60(m, 1H), 9.73 (br s)

Example 9

1-(6-Chloro-3-pyridylmethyl)amino-1-methylthio-2-nitroethylene (Compound 27)

To 100 ml of EtOH were added 2.4 g (1.5×10^{-2} mole) of 1,1-bis(methylthio)-2-nitroethylene and 1.4 g (9.8×10^{-3} mole) of 6-chloro-3-pyridylmethylamine and the mixture was refluxed for 2 hours. The EtOH was distilled off and the residue was subjected to silica gel column chromatography using CH_2Cl_2 as an eluent. The procedure gave 1.2 g of the title compound as a pale yellow solid.

NMR (DMSO-d_6) δ: 2.48 (s, 3 H), 4.71 (d, J = 6.7 Hz, 2 H), 6.66 (br s, 1 H), 7.50 (d, J = 8.8 Hz, 1 H), 7.84 (dd, J = 8.8 & 2.8 Hz, 1 H), 8.41 (d, J = 2.8 Hz, 1 H), 10.0-11.0 (br, 1 H)

Example 10

1-(6-Chloro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene (Compound 28)

In 100 ml of EtOH was dissolved 1.2 g (4.6×10^{-3} mole) of 1-(6-chloro-3-pyridylmethyl)amino-1-methylthio-2-nitroethylene and on reflux, a solution of 0.84 g of 40% aqueous methylamine in 30 ml EtOH was added dropwise over 1 hour. After cooling, the reaction mixture was concentrated under reduced pressure to about 50 ml and the resulting crystals were collected by filtration and dried to give 0.6 g of the title compound as pale yellow needles.

m.p.: 181-183 °C

NMR (DMSO-d_6) δ: 2.6-3.1 (m, 3 H), 4.47 (d, J = 6.3 Hz, 2 H), 6.45 (s, 1 H), 7.48 (d, J = 8.8 Hz, 1 H), 7.81 (dd, J = 8.8 & 2.7 Hz), 8.39 (d, J = 2.7 Hz, 1H), 9.5-10.4 (br, 1 H)

Example 11

1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 29)

(1) Using N-(6-chloro-3-pyridylmethyl)-N-methylamine, the procedure of Example 8 (1) was repeated to give N-(6-chloro-3-pyridylmethyl)-N-methyl-N'-methylthiourea as crystals.

m.p.: 109-110 °C

NMR ($CDCl_3$) δ: 3.06 (s, 3 H), 3.16 (d, J = 4.8 Hz, 3 H), 5.22 (s, 2H), 5.8-6.3 (br, 1 H), 7.30 (d, J = 8.6 Hz, 1H), 7.76 (dd, J = 8.6 & 2.7 Hz, 1H), 8.30 (d, J = 2.7 Hz, 1 H)

(2) Using the N-(6-chloro-3-pyridylmethyl)-N-methyl-N'-methylthiourea otained in (1), the procedure of Example 8 (2) was repeated to give S-methyl-N-(6-chloro-3-pyridylmethyl)-N-methyl-N'-methylisothiourea as oil.

NMR ($CDCl_3$) δ: 2.36 (s, 3 H), 2.94 (s, 3 H), 3.27 (s, 3 H), 4.63 (s, 2 H), 7.30 (d, J = 8.6 Hz, 1 H), 7.62 (dd, J = 8.6 & 2.7 Hz, 1 H), 8.31 (d, J = 2.7 Hz, 1 H)

(3) Using the S-methyl-N-(6-chloro-3-pyridylmethyl)-N-methyl-N'-methylisothiourea obtained in (2), the procedure of Example 8 (3) was repeated to give the title compound as crystals.

m.p.: 103-104 °C

NMR ($CDCl_3$) δ: 2.80 (s, 3 H), 3.07 (d, J = 4.8 Hz, 3 H), 4.38 (s, 2 H), 6.51 (s, 1 H), 7.37 (d, J = 8.6 Hz, 1 H), 7.58 (dd, J = 8.6 & 2.7 Hz, 1H), 8.31 (d, J = 2.7 Hz, 1 H), 9.5-9.9 (br, 1 H)

Example 12

1-Methoxy-1-(3-pyridylmethyl)amino-2-nitroethylene (Compound 30)

In one liter of MeOH was dissolved 16.5 g (0.1 mole) of 1,1-bis(methylthio)-2-nitroethylene with heating and on reflux, a solution of 11.0 g (0.1 mole) of 3-pyridylmethylamine in 200 ml of MeOH was added dropwise in 4 installments at 1-hour intervals. The mixture was further refluxed for 3 hours and the MeOH was distilled off. The residue was purified by silica gel column chromatography to give the title compound as white prisms. In this procedure, the compound 1-1 described in Example 1 was also produced as a byproduct.

m.p.: 129-130 °C

NMR ($CDCl_3$) δ: 3.86 (s, OMe), 4.60 (d, CH_2N), 6.68 (s, $=CHNO_2$), 10.15 (br, NH)

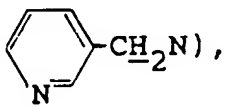
Example 13

1-[N-Ethyl-N-(3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene (Compound 31)

(1) In 50 ml of ethyl ether was dissolved 2.4 g of N-ethyl-N-(3-pyridylmethyl)amine followed by addition of 1.3 g of methyl isothiocyanate. The mixture was stirred at room temperature (25 °C) for 1 hour. The resulting precipitate was collected by filtration, washed with a small amount of ethyl ether and dried to give 3.7 g of N-methyl-N'-ethyl-N'-(3-pyridylmethyl)thiourea as white prisms.

m.p.: 122-123 °C

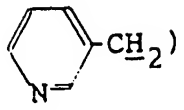
NMR ($CDCl_3$) δ: 1.16 (t, $CH_2\underline{CH_3}$), 3.16 (d, MeN), 3.55 (q, $\underline{CH_2}CH_3$), 5.12 (s,



5.95 (br s, NH)

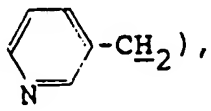
(2) In 30 ml of dry tetrahydrofuran was dissolved 3.1 g of the N-methyl-N'-ethyl-N'-(3-pyridylmethyl)-thiourea obtained in (1) followed by addition of 0.6 g of 60% sodium hydride. The mixture was stirred at room temperature (25 °C) for 1 hour. Then, 2.1 g of methyl iodide was added dropwise and the mixture was further stirred for 3 hours. The reaction mixture was concentrated and the residue was diluted with 50 ml of a saturated solution of sodium chloride and extracted 3 times with 50 ml portions of ethyl acetate. The extracts were pooled and dried over $MgSO_4$. The solvent was then distilled off to give 3.1 g of crude S-methyl-N-methyl-N'-ethyl-N'-(3-pyridylmethyl)isothiourea as a yellow oil.

NMR ($CDCl_3$) δ: 1.06 (t, $CH_2\underline{CH_3}$), 2.30 (s, MeS), 3.23 (s, MeN), 3.35 (q, $\underline{CH_2}CH_3$), 4.53 (s,



(3) To 2.2 g of the S-methyl-N-methyl-N'-ethyl-N'-(3-pyridylmethyl)isothiourea obtained in (2) was added 10 ml of nitromethane and the mixture was refluxed for 16 hours. The reaction mixture was concentrated and the residue was subjected to silica gel column chromatography using methanol-chloroform (1:5) as an eluent to give 1.4 g of the title compound as a yellow viscous oil.

NMR ($CDCl_3$) δ: 1.20 (t, $CH_2\underline{C}H_3$), 3.08 (d, MeN), 3.18 (q, $\underline{C}H_2CH_3$), 4.46 (s,



6.53 (s, = $CHNO_2$), 9.86(br s, NH)

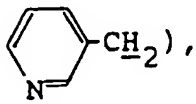
Example 14

1-[N-(2-Dimethoxyethyl)-N-(3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene (Compound 32)

Using N-(2-dimethoxyethyl)-N-(3-pyridylmethyl)amine in lieu of N-ethyl-N-(3-pyridylmethyl)amine, the steps (1), (2) and (3) of Example 13 were carried out to give the following compounds at the respective steps.

(1) N-Methyl-N'-(2-dimethoxyethyl)-N'-(3-pyridylmethyl)thiourea (pale yellow viscous oil)

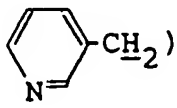
NMR ($CDCl_3$) δ: 3.13 (d, MeN), 3.37 (s, MeO), 3.53 (d, $N\underline{C}H_2CH$), 4.30 (t, $CH_2\underline{C}H$), 5.22 (s,



7.02 (br s, NH)

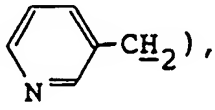
(2) S-Methyl-N-methyl-N'-(2-dimethoxyethyl)-N'-(3-pyridylmethyl)isothiourea (yellow oil)

NMR ($CDCl_3$) δ: 2.26 (s, MeS), 3.24 (s, MeN), 3.35 (s, MeO), 3.46 (d, $\underline{C}H_2CH$), 4.48 (t, $CH_2\underline{C}H$), 4.69 (s,



(3) Title compound (yellow viscous oil)

NMR ($CDCl_3$) δ: 1.20 (t, $CH_2\underline{C}H_3$), 3.08 (d, MeN), 3.18 (q, $\underline{C}H_2CH_3$), 4.46 (s,



6.53 (s, =$CHNO_2$), 9.86 (br s, NH)

Example 15

1-Ethylamino-1-[N-methyl-N-(3-pyridylmethy)]amino2-nitroethylene (compound 33)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and ethyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methyl isothiocyanate, respectively, to give the following compounds in the respective steps.

(1) N-ethyl-N'-methyl-N'-(3-pyridylmethyl)thiourea
m.p.:110-111 °C
NMR ($CDCl_3$) δ:1.23 (3 H, t, J=7.5 Hz), 3.05 (3 H, s), 3.5-3.9 (2 H, m), 5.20 (2 H, s), 5.8-6.2 (1 H, br), 7.26 (1 H, dd, J=8.4 & 5.4 Hz), 7.72 (1 H, dt, J=8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)
IR (Nujol): 3180 cm^{-1}

(2) S-Methyl-N-ethyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea (yellow oil)
NMR ($CDCl_3$) δ: 1.16 (3 H, t, J=7.5 Hz), 2.36 (3 H, s), 2.93 (3 H, s), 3.56 (2 H, q, J=7.5 Hz), 4.64 (2 H, s), 7.26 (1 H, dd, J=8.4 & 5.4 Hz), 7.63 (1 H, dt, J=8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)

(3) Title compound (viscous oil)
NMR ($CDCl_3$) δ: 1.34 (3 H, t, J=7.5 Hz), 2.82 (3 H, s), 3.1-3.6 (2 H, m), 4.43 (2 H, s), 6.52 (1 H, s), 7.32 (1 H, dd, J=8.4 & 5.4 Hz), 7.58 (1 H, dt, J=8.4 & 1.5 Hz), 3.4-8.7 (2 H, m), 9.3-9.8 (1 H, br)
IR (neat): 3220 cm^{-1}

Example 16

1-n-Butylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 34)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and n-butyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methylisothiocyanate, respectively, to give the following compounds in the respective steps.

(1) N-n-Butyl-N'-methyl-N'-(3-pyridylmethyl)thiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 0.93 (3 H, t, J=7.8 Hz), 1.2-1.9 (4 H, m), 3.06 (3 H, s), 3.4-3.9 (2 H, m), 5.21 (2 H, s), 5.5-6.1 (1 H, br), 7.28 (1 H, dd, J=8.4 & 5.4 Hz), 7.74 (1 H, dt, J=8.4 & 1.5 Hz), 8.4-8.7 (2 H, m)
IR (neat): 3270 cm^{-1}

(2) S-Methyl-N-n-butyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea (yellow oil)
NMR ($CDCl_3$) δ:0.90 (3 H, t, J=7.8 Hz), 1.1-1.9 (4 H, m), 2.30 (3 H, s), 2.85 (3 H, s), 3.49 (2 H, t, J=6.8 Hz), 4.56 (2 H, s), 7.23 (1 H, dd, J=8.4 & 5.4 Hz), 7.60 (1 H, dt, J=8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)

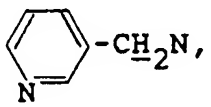
(3) Title compound (viscous oil)
NMR ($CDCl_3$) δ: 0.94 (3 H, t, J=7.8 Hz), 1.2-1.9 (4 H, m), 2.80 (3 H, s), 3.34 (2 H, m), 4.42 (2 H, s), 6.54 (1 H, s), 7.34 (1 H, dd, J=8.4 & 5.4 Hz), 7.58 (1 H, dt, J=8.4 & 1.5 Hz), 8.4-8.7 (2 H, m), 9.4-9.9 (1 H, br)
IR (neat): 3210 cm^{-1}

Example 17

1-Methylamino-1-[N-(2-methoxyethyl)-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 35)

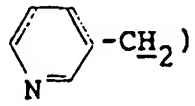
The steps (1), (2) and (3) of Example 13 were repeated except that N-(2-methoxyethyl)-N-(3-pyridylmethyl)amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-(2-methoxyethyl)-N'-(3-pyridylmethyl)thiourea (colorless viscous oil)
NMR ($CDCl_3$) δ: 3.33 (s, MeO), 3.50 (m, CH_2CH_2), 5.20 (s,

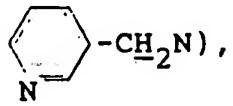


7.26 (br s, NH)

(2) S-Methyl-N-methyl-N'-(2-methoxyethyl)-N'-(3-pyridylmethyl)isothiourea (oil)
NMR ($CDCl_3$) δ: 2.27 (s, MeS), 3.23 (s, MeN), 3.30 (s, MeO), 3.52 (m, CH_2CH_2), 4.66 (s,



(3) Title compound (yellow viscous oil)
NMR ($CDCl_3$) δ: 3.06 (d, MeN), 3.35 (s, MeO), 3.43 (m, CH_2CH_2), 4.53 (s,



6.55 (s, $=CHNO_2$), 9.10 (br s, NH)

Example 18

1-Allylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 36)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and allyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methyl isothiocyanate, respectively, to give the following compounds in the respective steps.
(1) N-Allyl-N'-methyl-N'-(3-pyridylmethyl)thiourea
m.p.: 82-84 °C
NMR ($CDCl_3$) δ: 3.07 (3 H, s), 4.34 (2H, m), 5.0-5.4 (2H, m), 5.21 (2H, s), 5.6-6.3 (2 H, m), 7.27 (1 H, dd, J = 8.4 & 5.4 Hz), 7.73 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)
IR (Nujol): 3280 cm^{-1}
(2) S-Methyl-N-allyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea (yellow oil)
NMR ($CDCl_3$) δ: 2.30 (3 H, s), 2.90 (3 H, s), 4.1-4.3 (2 H, m), 4.62 (2 H, s), 4.9-5.3 (2 H, m), 5.7-6.3 (1 H, m), 7.26 (1 H, dd, J = 8.4 & 5.4 Hz), 7.62 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.7 (2 H, m)
(3) Title compound (oil)
NMR ($CDCl_3$) δ: 2.81 (3 H, s), 3.9-4.2 (2 H, m), 4.43 (2 H, s), 5.1-5.6 (2 H, m), 5.7-6.2 (1 H, m), 6.55 (1 H, s), 7.35 (1 H, dd, J = 8.4 & 5.1 Hz), 7.60 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.7 (2 H, m), 9.4-9.9 (1 H, br)

Example 19

1-iso-Propylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 37)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and iso-propyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methyl isothiocyanate, respectively, to give the following compounds in the respective steps.
(1) N-iso-Propyl-N'-methyl-N'-(3-pyridylmethyl)thiourea
m.p.: 135-136 °C
NMR ($CDCl_3$) δ: 1.26 (6 H, d, J = 6.3 Hz), 3.03 (3 H, s), 4.4-4.9 (1 H, m), 5.21 (2 H, s), 5.0-5.5 (1 H, br), 7.27 (1 H, dd, J = 8.4 & 5.1 Hz), 7.74 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.7 (2 H, m)
IR (Nujol): 3200 cm^{-1}
(2) S-Methyl-N-iso-propyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea (oil)
NMR ($CDCl_3$) δ: 1.07 (6 H, d, J = 6.3 Hz), 2.30 (3 H, s), 2.84 (3 H, s), 3.6-4.1 (1 H, m), 4.50 (2 H, s), 7.23 (1 H, dd, J = 8.4 & 5.1 Hz), 7.61 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)
(3) Title compound
m.p.: 119-121 °C
NMR ($CDCl_3$) δ: 1.31 (6 H, d, J = 6.6 Hz), 2.83 (3 H, s), 3.5-4.0 (1 H, m), 4.44 (2 H, s), 6.52 (1 H, s), 7.33 (1 H, dd, J = 8.4 & 5.1 Hz), 7.57 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.7 (2 H, m), 8.9-9.4 (1 H, br d, J = 9.6 Hz)

IR (Nujol): 3080 cm^{-1}

Example 20

1-Benzylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 38)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and benzyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methylisothiocyanate, respectively, to give the following compounds in the respective steps.

(1) N-Benzyl-N'-methyl-N'-(3-pyridylmethyl)thiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 3.03 (3 H, s), 4.90 (2 H, d, J = 5.1 Hz), 5.21 (2 H, s), 6.10 (1 H, br), 7.1-7.5 (6 H, m), 7.74 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.6 (2 H, m)
IR (neat): 3250 cm^{-1}

(2) S-Methyl-N-benzyl-N'-methyl-N'-(3-pyridylmethyl)isothiourea (oil)
NMR ($CDCl_3$) δ: 2.29 (3 H, s), 2.92 (3 H, s), 4.62 (2 H, s), 4.77 (2 H, s), 7.1-7.5 (6 H, m), 7.59 (1 H, dt, J = 8.4 & 1.5 Hz), 8.4-8.7 (2 H, m)

(3) Title compound (oil)
NMR ($CDCl_3$) δ: 2.78 (3 H, s), 4.36 (2 H, s), 4.53 (2 H, d, J = 6.0 Hz), 6.56 (1 H, s), 7.1-7.5 (7 H, m), 8.3 = 8.5 (1 H, m), 8.57 (1 H, dd, J = 5.2 & 1.5 Hz), 9.7-10.2 (1 H, br)

Example 21

1-Methylamino-1-[N-methyl-N-(3-quinolylmethyl)]amino-2-nitroethylene (Compound 39)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-quinolylmethyl)amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(3-quinolylmethyl)thiourea m.p.: 138-139 °C
NMR ($CDCl_3$) δ: 3.09 (s, $MeNCH_2$), 3.18 (d, J = 5 Hz, MeNH), 5.35 (s, NCH_2), 6.00 (br, NH), 7.4-7.9 (m, 3 H, quinoline-H_3), 8.0-8.2 (m, 2 H, quinoline-H_2), 3.33 (d, J = 2 Hz, 1 H, quinoline-H_1)
IR (Nujol): 3200, 1545, 1530, 1495, 1445, 1375, 1335, 1240, 1050 cm^{-1}

(2) S-Metyl-N-metyl-N'-methyl-N'-(3-quinolylmethyl)isothiourea (oil)
NMR ($CDCl_3$) δ: 2.33 (s, MeS), 2.89 (s, $MeNCH_2$), 3.28 (s, MeN =), 4.73 (s, NCH_2), 7.2-7.9 (m, 3 H, quinoline-H_3), 7.9-8.2 (m, 2 H, quinoline-H_2), 8.85 (d, J = 2 Hz, 1 H, quinoline-H_1)
IR (neat): 1600, 1490, 1370, 1340, 1060, 1020, 755 cm^{-1}

(3) Title compound
m.p.: 145-157 °C
NMR ($CDCl_3$) δ: 2.85 (s, $MeNCH_2$), 3.08 (d, J = 6 Hz, MeNH), 4.58 (s, NCH_2), 6.59 (s, $=CHNO_2$), 7.5-7.95 (m, 3 H, quinoline-H_3), 7.95-8.25 (m, 2 H, quinoline-H_2), 8.81 (d, J = 2 Hz, 1 H, quinoline-H_1), 9.80 (br, NH)
IR (Nujol): 1590, 1545, 1405, 1310, 1280, 1230 cm^{-1}

Example 22

1-Metylamino-1-[N-methyl-N-[1-(3-pyridyl)ethyl]]amino-2-nitroethylene (Compound 40)

The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-[1-(3-pyridyl)ethyl]amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-[1-(3-pyridyl)ethyl]thiourea (pale yellow viscous oil)
NMR $CDC1_3$) δ: 1.56 (d, J = 7 Hz, MeCH), 2.76 (s, $MeNCH_2$), 3.18 (d, J = 5 Hz, MeNH), 6.30 (br, NH), 7.04 (q, J = 7 Hz, MeCH), 7.28 (dd, J = 7 and 5 Hz, 1 H, pyridine-H_1), 7.70 (m, 1 H pyridine-H_1), 8.5 (m, 2 H, pyridine-H_2)
IR (neat): 3270, 1550 (sh.), 1530, 1480, 1420, 1375, 1340, 1295 cm^{-1}

(2) S-Methyl-N-methyl-N'-methyl-N'-[1-(3-pyridyl)ethyl]thiourea (oil)
NMR ($CDCL_3$) δ: 1.54 (d, J = 7 Hz, MeCH), 2.31 (s, MeS), 2.63 (s, $MeNCH_2$), 3.27 (s, MeN =), 5.66 (q, J = 7 Hz, MeCH), 7.24 (dd, J = 5 & 8 Hz, 1 H, pyridine-H_1), 7.62 (m, 1 H, pyridine-H_1), 8.48 (dd, J = 5 & 2 Hz, 1 H, pyridine-H_1), 8.59 (d, J = 2 Hz, 1 H, pyridine-H_1)

IR (neat): 2910, 1600, 1415, 1390, 1370, 1235, 1070, 1010, 710 cm^{-1}

(3) Title compound (viscous oil)

NMR ($CDCl_3$) δ: 1.70 (d, J=7 Hz, MeCH), 2.63 (S, MeN), 3.02 (d, J=5 Hz, MeNH), 4.93 (q, J=7 Hz, MeCH), 6.50 (s, $=CHNO_2$), 7.33 (dd, J=5 & 8 Hz, 1 H, pyridine-H_1), 7.60 (m, 1 H, pyridine-H_1), 8.6 (m, 2 H, pyridine-H_2), 9.77 (br, NH)

IR (neat): 1585, 1420, 1400, 1340, 1240, 1020, 750 cm^{-1}

Example 23

1-[2,2-Dimethyl-1-(3-pyridylmethyl)]hydrazino-1-methylamino-2-nitroethylene (Compound 41)

(1) In 30 ml of toluene was dissolved 2.5 g of 1,1-dimethyl-2-(3-pyridylmethyl)hydrazine followed by addition of 1.2 g of methyl isothiocyanate and the mixture was refluxed for 1 hour. The reaction mixture was concentrated and the resulting crystals are collected by filtration, washed with ethyl ether and dried. The procedure gave 2.6 g of 1,1-dimethyl-4-methyl-2-(3-pyridylmethyl)thiosemicarbazide as white prisms.

m.p.: 101-102 °C

NMR ($CDCl_3$) δ: 2.45 (s, Me_2N), 3.17 (d, J=5 Hz, MeNH), 5.28 (s, CH_2N), 7.20 (dd, J=8 and 5 Hz, 1 H, pyridine-H_1), 7.89 (m, 1 H, pyridine-H_1), 8.10 (br, NH), 8.50 (dd, J=5 & 2 Hz, 1 H, pyridine-H_1), 8.62 (d, J=2 Hz, 1 H, pyridine-H_1)

IR (Nujol): 3200, 1514, 1420, 1370, 1320, 975 cm^{-1}

(2) 0.52 g of 60% sodium hydride was washed with petroleum ether and suspended in 20 ml of dry tetrahydrofuran, followed by addition of 2.9 g of 1,1-dimethyl-4-methyl-2-(3-pyridylmethyl)-thiosemicarbazide as prepared according to (1). The mixture was stirred at 50 °C for 2 hours. After cooling and addition of 1.8 g of methyl iodide, the mixture was stirred at room temperature (25 °C) for 2 hours and, then, concentrated. To the residue was added 50 ml of ethyl acetate and the insoluble matter was filtered off. The filtrate was dried over $MgSO_4$ and concentrated to give 2.2 g of S-methyl-1,1-dimethyl-4-methyl-2-(pyridylmethyl)isothiosemicarbazide as oil.

NMR ($CDCl_3$) δ: 2.41 (s, MeS), 2.60 (s, Me_2N), 3.06 (s, MeN), 4.30 (s, CH_2N), 7.18 (dd, J=5 & 8 Hz, 1 H, pyridine-H_1), 7.60 (m, 1 H, pyridine-H_1), 8.10 (dd, J=5 & 2 Hz, 1 H, pyridine-H_1), 8.21 (d, J=2 Hz, pyridine-H_1)

IR (neat): 1600, 1420, 1240, 1020, 710 cm^{-1}

(3) To 2.2 g of S-methyl-1,1-dimethyl-4-methyl-2-(pyridylmethyl)isothiosemicarbazide prepared in (2) was added 10 ml of nitromethane and the mixture was refluxed for 7 hours. The reaction mixture was concentrated and subjected to silica gel column chromatography using chloroform-methanol (5:1) as an eluent. The procedure gave 1.0 g of the title compound as yellow prisms.

m.p.: 109-110 °C

NMR ($CDCl_3$) δ: 2.62 (s, Me_2N), 3.16 (d, J=6 Hz, MeN), 4.43 (s, CH_2N), 6.43 (s, $=CHNO_2$), 7.27 (dd, J=8 & 5 Hz, 1 H, pyridine-H_1), 7.60 (m, 1 H, pyridine-H_1), 8.5-8.65 (m, 2 H, pyridine-H_2), 10.1 (br, NH)

IR (Nujol): 1585, 1405, 1340, 1315, 1235 cm^{-1}

Example 24

1-Methylamino-1-[N-(n-propyl)-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 42)

The steps (1), (2) and (3) of Example 13 were repeated except that N-n-propyl-N-(3-pyridylmethyl)-amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-(n-propyl)-N'-(3-pyridylmethyl)thiourea (pale yellow viscous oil)

NMR ($CDCl_3$) δ: 0.90 (t), 1.4-1.9 (m), 3.16 (d. MeN), 3.42 (t), 5.15 (s), 5.87 (br s, NH), 7.26 (dd), 7.74 (dt), 8.46-8.60 (m, 2 H)

IR (neat): 3270, 1525, 1340, 1235, 1020, 710 cm^{-1}

(2) S-Methyl-N-methyl-N'-(n-propyl)-N'-(3-pyridylmethyl)isothiourea (yellow oil)

NMR ($CDCl_3$) δ: 0.84 (t), 1.33-1.80 (m), 2.29 (s, MeS), 3.23 (s, MeN), 3.26 (t), 4.55 (s), 7.22 (dd), 7.56 (dt), 8.43-8.60 (m, 2 H)

IR (neat): 1600, 1425, 1210, 715 cm^{-1}

(3) Title compound (yellow viscous oil)

NMR ($CDCl_3$) δ: 0.86 (t), 1.40-1.90 (m, 2 H), 2.95-3.30 (m, 2 H), 3,05 (d, MeN), 4.53 (s, 2 H), 6.55 (s, $=CHNO_2$), 7.34 (dd), 7.66 (dt), 8.43-8.66 (m, 2 H), 9.56 (br d, NH)

Example 25

1-[N-(n-Butyl-N-(3-pyridyl)]amino-1-methylamino-2-nitroethylene (Compound 43)

The steps (1), (2) and (3) of Example 13 were repeated except that N-(n-butyl)-N-(3-pyridylmethyl)-amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(n-Butyl)-N-(3-pyridylmethyl)-N'-methylthiourea (pale yellow viscous oil)

NMR ($CDCl_3$) δ: 0.90 (t), 1.1-1.8 (m, 4 H), 3.15 (d, MeN), 3.30-3.56 (m), 5.13 (s), 5.82 (br s, NH), 7.25 (dd), 7.73 (dt), 8.43-8.60 (m, 2 H)

IR (neat): 3280, 1525, 1345, 1230, 1030, 710 cm^{-1}

(2) S-Methyl-N-methyl-N'-(n-butyl)-N'-(3-pyridylmethylisothiourea (yellow oil)

NMR ($CDCl_3$) δ: 0.86 (t), 1.03-1.70 (m, 4 H), 2.28 (s, MeS), 3.23 (s, MeN), 3.30 (t), 4.54 (s), 7.22 (dd), 7.56 (dt), 8.40-8.56 (m, 2 H)

IR (neat): 1605, 1425, 1190, 1020, 715 cm^{-1}

(3) Title compound (viscous oil)

NMR ($CDCl_3$) δ: 0.90 (t), 1.06-1.80 (m, 4 H), 2.96-3.23 (m, 2 H), 3.07 (d, MeN), 4.40 (s), 6.56 (s, $=CHNO_2$), 7.33 (dd), 7.60 (dt), 8.46-8.66 (m, 2 H), 9.82 (br d, NH)

Example 26

1-[N-Benzyl-N-(3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene (Compound 44)

The steps (1), (2) and (3) of Example 13 were repeated except that N-benzyl-N-(3-pyridylmethyl)amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Benzyl-N-(3-pyridylmethyl)-N'-methylthiourea

m.p.: 141-143 °C (white prisms)

(2) S-Methyl-N-methyl-N'-benzyl-N'-(3-pyridylmethyl)isothiourea (yellow oil)

NMR ($CDCl_3$) δ: 2.32 (s, MeS), 3.26 (s, MeN), 4.45 (s), 4.52 (s), 7.06-7.36 (m, 6 H), 7.50 (dt), 8.36-8.53 (m, 2 H)

IR (neat): 1600, 1425, 1180, 1020, 700 cm^{-1}

(3) Title compound

m.p.: 118-119 °C (pale yellow scales)

NMR ($CDCl_3$) δ: 3.16 (d, J = 5 Hz, MeN), 4.22 (s, CH_2 and CH_2), 6.53 (s, $=CHNO_2$), 7.06-7.60 (m, 7 H), 8.40 (br s), 8.60 (br d), 9.76 (br d, J = 5 Hz, NH)

IR (Nujol): 1590, 1520, 1450, 1360, 1280 cm^{-1}

Example 27

1-Amino-1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-2-nitroethylene (Compound 45)

(1) In 200 ml of EtOH was dissolved 5.0 g of 1,1-bis(methylthio)-2-nitroethylene with heating and a solution containing 4.7 g of N-(6-chloro-3-pyridylmethyl)-N-methylamine in 50 ml of EtOH was added dropwise on reflux in 3 portions at 30-minute intervals. After completion of dropwise addition, the mixture was further refluxed for 3 hours and the EtOH was then distilled off. The residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (20:1) as an eluent. The procedure gave 3.5 g of 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylthio-2-nitroethylene as a yellow viscous oil.

NMR ($CDCl_3$) δ: 2.46 (s, MeS), 3.03 (s, MeN), 4.76 (s, CH_2), 6.76 (s, $=CHNO_2$), 7.35 (d), 7.60 (dd), 8.30 (d)

IR (neat): 1750, 1540, 1260, 1100, 1020 cm^{-1}

(2) In 20 ml of MeOH was dissolved 1.1 g of 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylthio-2-nitroethylene prepared in (1), followed by addition of 1.0 ml of 25% aqueous ammonia, and the mixture was stirred at room temperature for 1 hour. The resulting crystals were collected by filtration,

washed with a small amount of MeOH and dried to give 0.85 g of the title compound as pale yellow scales.

m.p.: 206-207 °C

NMR (DMSO-d_6) δ: 3.03 (s, MeN), 4.65 (s, CH_2), 6.60 (s, $=CHNO_2$), 7.45 (d), 7.68 (dd), 8.31 (d), 8.92 (br s, NH_2)

IR (Nujol): 3280, 3140, 1625, 1580, 1420, 1225 cm^{-1}

Example 28

1-(6-Chloro-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene (Compound 46)

(1) In 50 ml of EtOH was dissolved 3.3 g of 1,1-bis(methylthio)-2-nitroethylene and 2.2 ml of a 40% aqueous solution of dimethylamine was added dropwise in 2 portions at 30-minute intervals under refluxing. After completion of dropwise addition, the mixture was further refluxed for 30 minutes. Then, the EtOH was distilled off and the residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (20:1) as an eluent. The procedure gave 1.0 g of 1-dimethylamino-1-methylthio-2-nitroethylene as a yellow oil.

NMR ($CDCl_3$) δ: 2.46 (s, 3 H), 3.21 (s, 6 H), 6.69 (s, 1 H)

(2) The 1-dimethylamino-1-methylthio-2-nitroethylene (1.0 g) prepared in (1) and 1.0 g of 6-chloro-3-pyridylmethylamine were refluxed in 30 ml of EtOH for 2 hours. The EtOH was then distilled off and the residue was subjected to silica gel column chromatography using $CHCl_3$-MeOH (10:1) as an eluent. The crystals obtained were recrystallized from EtOH to recover 0.82 g of the title compound as pale yellow crystals.

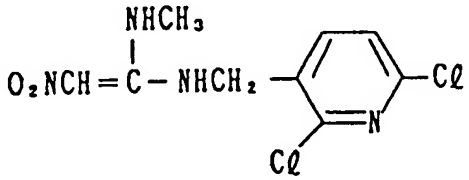
m.p.: 124-125 °C

NMR ($CDCl_3$) δ: 2.99 (s, 6 H), 4.53 (d, J = 5.4 Hz, 2 H), 6.46 (s, 1 H), 7.34 (d, J = 8.4 Hz, 1 H), 7.72 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.35 (d, J = 2.4 Hz, 1 H), 9.2-9.8 (br, 1 H)

IR (Nujol): 1585, 1440, 1380, 1260 cm^{-1}

Example 29

1-(2,6-Dichloro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene (Compound 47)



A mixture of 1.2 g (0.007 mole) of (2,6-dichloro-3-pyridylmethyl)amine and 1 g (0.007 mole) of 1-methylamino-1-methylthio-2-nitroethane was refluxed in 50 ml of EtOH for 6 hours. After cooling, the reaction mixture was concentrated and the resulting crystals were collected by filtration, washed with CH_2Cl_2 and a small amount of EtOH in that order and dried. The procedure gave 0.53 g of the title compound as a white powder.

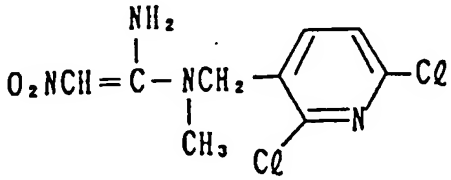
m.p.: 211-213 °C (decompn.)

NMR (DMEO-d_6) δ: 2.83 (br, 3 H), 4.50 (br d, 2 H), 6.43 (s, 1 H), 7.58 (d, J = 8.5 Hz), 7.80 (d, J = 8.5 Hz), 7.0-7.93 (br, NH), 9.50-10.50 (br, NH)

IR (Nujol): 3170, 1630, 1580, 1375, 1210 cm^{-1}

Example 30

1-Amino-1-[N-(2,6-dichloro-3-pyridylmethyl)-N-methyl]amino-2-nitroethylene (Compound 48)



In 30 ml of MeOH was dissolved 0.9 g (0.003 g mole) of 1-[N-(2,6-dichloro-3-pyridylmethyl)-N-methyl]-amino-1-methylthio-2-nitroethylene, followed by addition of 0.6 ml (0.0045 mole) of 25% aqueous ammonia at 50 °C, and the mixture was stirred at the same temperature for 1 hour. After cooling, the reaction mixture was concentrated and the resulting crystals were collected by filtration, washed with a small amount of EtOH and dried. The procedure gave 0.7 g of the title compound as a white powder.

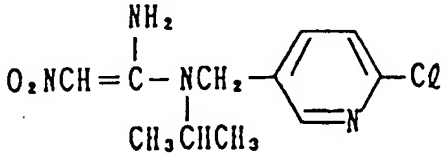
m.p.: 214-215 °C (decompn.)

NMR (DMSO-d_6) δ: 3.05 (s, 3 H), 4.63 (s, 2 H), 6.56 (s, 1 H), 7.46-7.70 (m, 2 H), 8.90 (br s, NH_2)

IR (Nujol): 3350, 1610, 1565, 1410, 1290, 1220 cm^{-1}

Example 31

1-Amino-1-[N-(6-chloro-3-pyridylmethyl)-N-i-propyl]amino-2-nitroethylene (Compound 49)



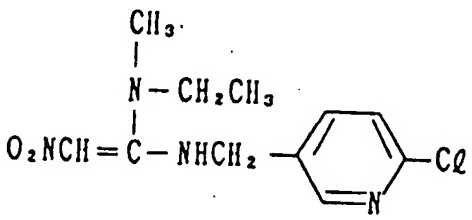
In 8 ml of EtOH was dissolved 0.59 g (0.00196 mole) of 1-[N-(6-chloro-3-pyridylmethyl)-N-1-propyl]-amino-1-methylthio-2-nitroethylene, followed by addition of 0.20 ml of 25% aqueous ammonia. The mixture was stirred at room temperature for 2 hours and 40 minutes. The reaction mixture was concentrated and the residue was subjected to silica gel (100 g) column chromatography using MeOH-$CHCl_3$ (1:7) as an eluent to give the title compound as oil. The oil was triturated with Et_2O and the resulting powder was collected by filtration, washed with Et_2O and dried. The procedure gave 0.19 g of the title compound.

NMR (DMSO-d_6) δ: 1.13 (d, J = 7 Hz, Me_2CH), 4.30 (septet, J = 7 Hz, Me_2CH), 4.62 (s, CH_2), 6.50 (s, $=CHNO_2$), 7.49 (d, J = 8 Hz, 1 H), 7.69 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H), 9.04 (br, NH_2)

IR (Nujol): 1610, 1540, 1280, 1230, 1100 cm^{-1}

Example 32

1-(6-Chloro-3-pyridylmethyl)amino-1-(N-ethyl-N-methyl)amino-2-nitroethylene (Compound 50)



The step (2) of Example 28 was repeated except that 1-(N-ethyl-N-methyl)amino-1-methylthio-2-nitroethylene was used in lieu of 1-dimethylamino-1-methylthio-2-nitroethylene to give the title compound as pale yellow crystals.

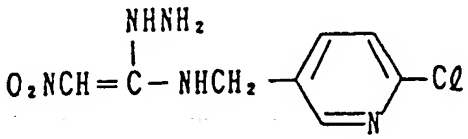
m.p.: 87-88 °C

NMR ($CDCl_3$) δ: 1.18 (t, J = 6.5 Hz, 3 H), 2.89 (s, 3 H), 3.23 (q, J = 6.5 Hz, 2 H), 4.46 (d, J = 5.7 Hz, 2 H), 6.53 (s, 1 H), 7.34 (d, J = 8.4 Hz, 1 H), 7.69 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.33 (d, J = 2.4 Hz, 1 H), 9.5-10.0 (br, 1 H)

IR (Nujol): 1600, 1460 cm^{-1}

Example 33

1-(6-Chloro-3-pyridylmethyl)amino-1-hydrazino-2-nitroethylene (Compound 51)



The reaction procedure of Example 3 was repeated except that 1-(6-chloro-3-pyridylmethyl)amino-1-methylthio-2-nitroethylene and hydrazine hydrate were used in lieu of 1-methylthio-1-(3-pyridylmethyl)-amino-2-nitroethylene and aqueous methylamine solution, respectively. The procedure gave the title compound as pale yellow crystals.

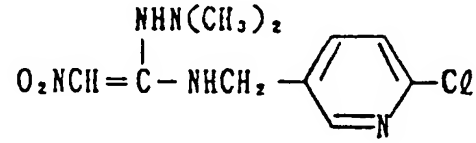
m.p.: 188-190 °C (decompn.)

NMR (DMSO-d_6) δ: 4.43 (br s, 2 H), 4.3-5.2 (br, 2 H), 6.49 (s, 1 H), 7.50 (d, J = 8.4 Hz, 1 H), 7.81 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.39 (d, J = 2.4 Hz, 1 H), 9.9-10.8 (br, 1 H)

IR (Nujol): 3260, 1650, 1560, 1450 cm^{-1}

Example 34

1-(6-Chloro-3-pyridylmethyl)amino-1-(2,2-dimethyl1-hydrazino)-2-nitroethylene (Compound 52)



The reaction procedure of Example 6 was repeated except that 6-chloro-3-pyridylmethylamine was used in lieu of 3-pyridylmethylamine to give the title compound as pale brown prisms.

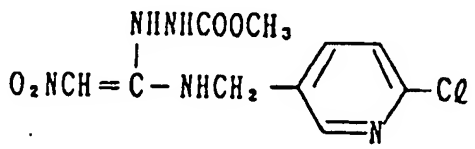
m.p.: 170-172 °C

NMR (DMSO-D_6) δ: 2.59 (S, 6 H), 4.43 (d, J = 6.6 Hz, 2 H), 6.2-6.7 (br, 1 H), 7.47 (d, J = 8.4 Hz, 1 H), 7.79 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.38 (d, J = 2.4 Hz, 1 H), 8.0-8.5 (br, 1 H), 9.9-10.5 (br, 1 H)

IR (Nujol): 3200, 1590, 1560, 1460, 1390, 1350 cm^{-1}

Example 35

1-(6-Chloro-3-pyridylmethyl)amino-1-(2-methoxycarbonyl)hydrazino-2-nitroethylene (Compound 53)



To a solution of 0.4 g (0.0016 mole) of 1-(6-chloro-3-pyridylmethyl)amino-1-hydrazino-2-nitroethylene in 15 ml of DMF was added 0.14 ml (0.0018 mole) of methyl chloroformate and the mixture was stirred at room temperature for 30 minutes. The DMF was distilled off under reduced pressure and the residue was subjected to silica gel column chromatography using EtOH-$CHCl_3$ (1:7) as an eluent. The procedure gave 0.14 g of the title compound as a pale yellow solid.

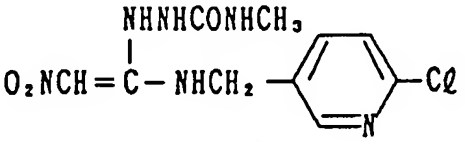
m.p. : 198-201 °C (decompn.)

NMR (DMSO-d_6) δ: 3.67 (s, 3 H), 4.48 (br d, J = 6 Hz, 2 H), 6.43 (s, 1 H), 7.52 (d, J = 8.4 Hz, 1 H), 7.80 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.38 (d, J = 2.4 Hz, 1 H), 9.1-9.6 (br, 1H), 10.0-10.9 (br, 1 H)

IR (Nujol): 3110, 1740, 1570, 1455 cm^{-1}

Example 36

1-(6-Chloro-3-pyridylmethyl)amino-1-(2-methylaminocarbonyl)hydrazino-2-nitroethylene (Compound 54)



To a solution of 0.3 g (0.0012 mole) of 1-(6-chloro-3-pyridylmethyl)amino-1-hydrazino-2-nitroethylene in 5 ml of DMF was added 0.15 ml (0.0025 mole) of methyl isocyanate and the mixture was allowed to stand at room temperature for 2 hours. The DMF was distilled off under reduced pressure and the residue was purified by silica gel column chromatography. The procedure gave 0.08 g of the title compound as a white solid.

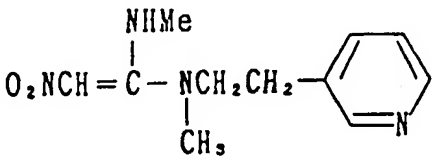
m.p.: 190-192 °C (decompn.)

NMR (DMSO-d_6) δ: 2.63 (d, J = 4.5 Hz, 3 H), 4.49 (br d, J = 6.0 Hz, 2 H), 6.47 (s, 1 H), 6.5-6.8 (br d, J = 4.5 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 1 H), 7.82 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.10 (s, 1 H), 8.40 (d, J = 2.4 Hz, 1 H)

IR (Nujol): 3200, 1680, 1550, 1455, 1380 cm^{-1}

Example 37

1-Methylamino-1-[N-methyl-N-[2-(3-pyridyl)ethyl]amino]-2-nitroethylene (Compound 55)



The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-[2-(3-pyridyl)ethyl]-amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-[2-(3-pyridyl)ethyl]thiourea

m.p.: 104-105 °C

NMR ($CDCl_3$) δ: 3.02 (m, CH_2-pyridine), 3.04 (s, $MeNCH_2$), 4.10 (m, CH_2N), 5.90 (br d, J = 5 Hz, NH), 7.26 (dd, J = 5 & 8 Hz, 1 H), 7.67 (m, 1 H), 8.50 (m, 2 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-[2-(3-pyridyl)ethyl]isothiourea (yellow brown oil)

(Note: After addition of 60% sodium hydride (oil), the mixture was stirred at 50 °C for 1 hour.)

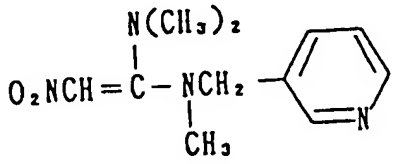
NMR ($CDCl_3$) δ: 2.15 (s, MeS), 2.84 (m, CH_2-pyridine), 2.93 (s, $MeNCH_2$), 3.21 (s, MeN=), 3.61 (m, NCH_2), 7.20 (dd, J = 5 & 8 Hz, 1 H), 7.53 (m, 1 H), 8.45 (m, 2 H)

(3) Title compound (yellow viscous oil)

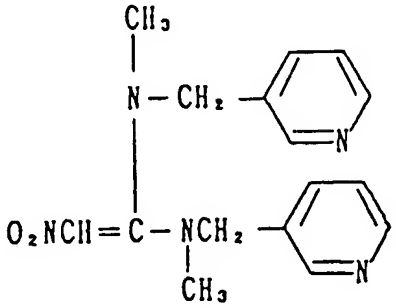
NMR ($CDCl_3$) δ: 2.93 (d, J = 5 Hz, MeNH), 2.96 (s, $MeNCH_2$), 2.97 (m, CH_2-pyridine), 3.50 (m, $MeNCH_2$), 6.52 (s, $=CHNO_2$), 7.27 (dd, J = 5 & 8 Hz, 1 H), 7.57 (m, 1 H), 8.50 (m, 2 H), 9.67 (br, NH)

Example 38

1-Dimethylamino-1-(N-methyl-N-3-pyridylmethyl)amino-2-nitroethylene (Compound 56) and 1,1-bis(N-methyl-N-3-pyridylmethyl)amino-2-nitroethylene (Compound 57)



(Compound 56)



(Compound 57)

A mixture of 2.0 g (0.012 mole) of 1-dimethylamino-1-methylthio-2-nitroethylene and 1.5 g (0.012 mole) of N-methyl-N-3-pyridylmethylamine was stirred at 120 °C for 40 minutes. The reaction mixture was subjected to column chromatography, elution being carrid out with MeOH-$CHCl_3$ (1:10) to give two fractions containing the desired compounds, respectively. One of the fractions was further purified by silica gel column chromatography using MeOH-$CHCl_3$ (1:10) and acetone-$CHCl_3$ (2:1) in succesion, whereby 0.40 g of the title compound (Compound 56) was obtained as pale yellow crystals. The other fraction was also chromatographed on a silica gel column and eluted with MeOH-$CHCl_3$ (1:10) and acetone-$CHCl_3$ (2:1) in that order to give 0.35 g of the title compound (Compound 57) as a yellow oil.

(Compound 56)

m.p.: 103-105 °C

NMR ($CDCl_3$) δ: 2.81 (s, 3 H), 2.98 (s, 6 H), 4.44 (s, 3 H), 6.41 (s, 1 H), 7.33 (dd, J = 8.4 & 5.1 Hz, 1 H), 7.64 (dt, J = 8.4 & 1.5 Hz, 1 H), 8.4-8.7 (m, 2 H)

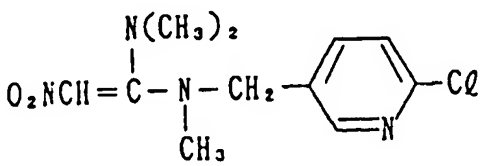
IR (Nujol): 1545, 1520, 1450, 1300, 1265 cm^{-1}

(Compound 57)

NMR ($CDCl_3$) δ: 2.83 (s, 6 H), 4.48 (s, 4 H), 6.52 (s, 1 H), 7.34 (dd, J = 8.4 & 5.1 Hz, 2 H), 7.62 (dt, J = 8.4 & 1.5 Hz, 2 H), 8.4-8.8 (m, 4H)

Example 39

1-[N-(6-Chloro-3-pyridylmethyl)-N-methyl]amino-1-dimethylamino-2-nitroethylene (Compound 58)



A mixture of 1.6 g (0.0099 mole) of 1-dimethylamino-1-methylthio-2-nitroethylene and 1.4 g (0.0089 mole) of N-(6-chloro-3-pyridylmethyl)-N-methylamine was stirred at 80 °C for 3 hours. The reaction mixture

was subjected to silica gel column chromatography using MeOH-$CDCl_3$ (1:10) twice and acetone-$CHCl_3$ - (2:1) once to give 0.33 g of the title compound as pale yellow crystals.

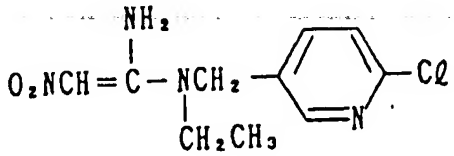
m.p.: 110-112 °C

NMR ($CDCl_3$) δ: 2.79 (s, 3 H), 2.97 (s, 6 H), 4.40 (s, 2 H), 6.38 (s, 1 H), 7.36 (d, J = 8.4 Hz, 1 H), 7.72 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.30 (d, J = 2.4 Hz, 1 H)

IR (Nujol): 1545, 1520, 1460, 1300, 1260 cm^{-1}

Example 40

1-Amino-1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-2-nitroethylene (Compound 59)



(1) In 200 ml of EtOH was dissolved 9.68 g of 1,1-bis(methylthio)-2-nitroethylene with heating, and a solution of 6.66 g (0.039 mole) of N-(6-chloro-3-pyridylmethyl)-N-ethylamine in 30 ml of EtOH was added dropwise on reflux. After 45 hours of refluxing, the EtOH was distilled off and the residue was subjected to silica gel (420 g) column chromatography using EtOH-$CHCl_3$ (1:20) as an eluent. The procedure gave 2.28 g of crude 1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylthio-2-nitroethylene as a brown oil.

NMR ($CDCl_3$) δ: 1.24 (t, J = 7 Hz, CH_2CH_3), 2.46 (s, MeS), 3.52 (q, J = 7 Hz, CH_2CH_3), 4.72 (s, CH_2-pyridine), 6.82 (s, $=CHNO_2$), 7.31 (d, J = 8 Hz, 1 H), 7.57 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H)

(2) In 30 ml of EtOH was dissolved 2.16 g of crude 1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylthio-2-nitroethylene prepared in (1), followed by addition of 0.766 ml of 25% aqueous ammonia. The mixture was stirred at room temperature for 3 hours. The solvent was distilled off and the residue was subjected to silica gel (200 g) column chromatography, elution being carried out with MeOH-$CHCl_3$ - (1:5). The procedure gave 0.69 g of the title compound as a pale yellow viscous oil. This product was triturated with ether, filtered and dried to give 0.57 g of the title compound as white powdery crystals.

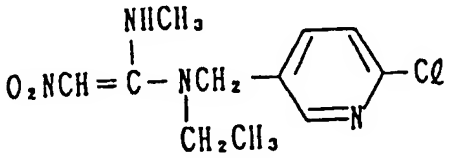
m.p.:159-161 °C

NMR ($CDCl_3$-DMSO-d_6 [4:1]) δ: 1.22 (t, J = 7 Hz, CH_2CH_3), 3.43 (q, CH_2CH_3), 4.62 (s, CH_2-pyridine), 6.61 (s, $=CHNO_2$), 7.35 (d, J = 8 Hz, 1 H), 7.62 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H), 8.97 (br, NH_2)

IR (Nujol): 1610, 1565, 1455, 1445, 1305, 1235 cm^{-1}

Example 41

1-[N-(6-Chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene (Compound 60)



The steps (1), (2) and (3) of Example 37 were repeated except that N-(6-chloro-3-pyridylmethyl)-N-ethylamine was used in lieu of N-methyl-N-[2-(3-pyridyl)ethyl]amine to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N-ethyl-N'-methylthiourea (yellow crystals)

m.p.: 133-134 °C

NMR ($CDCL_3$) δ: 1.16 (t, J = 7 Hz, CH_2CH_3), 3.15 (d, J = 5 Hz, MeN), 3.50 (q, J = 7 Hz, CH_2CH_3), 5.12 (s, CH_2-pyridine), 5.84 (br d, J = 5 Hz, NH), 7.30 (d, J = 8 Hz, 1 H), 7.80 (dd, J = 8 & 2 Hz, 1 H), 8.27 (d, J = 2 Hz, 1 H)

(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methylisothiourea (yellow brown oil)

NMR ($CDCl_3$) δ:1.09 (t, J = 7 Hz, CH_2CH_3), 2.29 (s, MeS), 3.21 (s, MeN =), 3.3 (q, J = 7 Hz, CH_2CH_3), 4.49 (s, CH_2-pyridine), 7.27 (d, J = 8 Hz, 1 H), 7.61 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H)

(3) Title compound (white crystals)

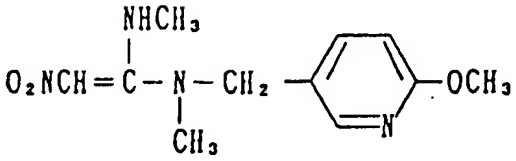
m.p.: 83-84 °C

NMR ($CDCl_3$) δ: 1.20 (t, J = 7 Hz, CH_2CH_3), 3.08 (d, J = 5 Hz, MeNH), 3.18 (q, J = 7 Hz, CH_2CH_3), 4.40 (s, CH_2-pyridine), 6.54 (s, $=CHNO_2$), 7.39 (d, J = 8 Hz, 1 H), 7.63 (dd, J = 8 & 2 Hz, 1 H), 8.33 (d, J = 2 Hz, 1 H), 9.79 (br d, J = 5 Hz, NH)

IR (Nujol): 1595, 1530, 1455, 1340, 1270, 1240 cm^{-1}

Example 42

1-[N-(6-Methoxy-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 61)



In 20 ml of DMF was dissolved 0.67 g (0.0026 mole) of 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene followed by addition of 1.00 g of a 28% solution of sodium methoxide in methanol. The mixture was stirred at 100 °C for 5.5 hours. The methanol and DMF were distilled off and the residue was diluted with aqueous sodium chloride solution and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and the CH_2Cl_2 was distilled off. The residue was subjected to silica gel (230 g) column chromatography using MeOH-$CHCl_3$ (1:5) as an eluent to give 0.22 g of a brown viscous oil. A small amount of ether was added to the oil and the mixture was cooled and triturated. The resulting crystals were diluted with ether, filtered and dried to give 0.128 g of the title compound as white - pale brown crystals.

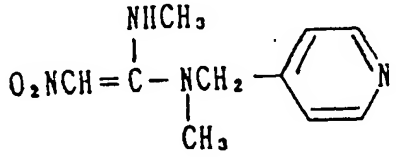
m.p.: 77-78 °C

NMR ($CDCl_3$) δ: 2.75 (s, MeN), 3.07 (d, J = 5 Hz, MeNH), 3.93 (s, OMe), 4.30 (s, CH_2-pyridine), 6.53 (s, $=CHNO_2$), 6.78 (d, J = 8 Hz, 1 H), 7.45 (dd, J = 8 & 2 Hz, 1 H), 8.05 (d, J = 2 Hz, 1 H), 9.80 (br, NH)

IR (Nujol): 1605, 1455, 1310, 1250, 1025 cm^{-1}

Example 43

1-Methylamino-1-[N-methyl-N-(4-pyridylmethyl)]amino-2-nitroethylene (Compound 62)



The steps (1), (2) and (3) of Example 37 were repeated except that N-methyl-N-(4-pyridylmethyl)amine was used in lieu of N-methyl-N-[2-(3-pyridyl)ethyl]amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(4-pyridylmethyl)thiourea

m.p.: 123-124 °C

NMR ($CDCl_3$) δ: 3.07 (s, $MeNCH_2$), 3.16 (d, J = 5 Hz, MeNH), 5.19 (s, CH_2), 6.29 (br d, J = 5 Hz, NH), 7.19 (m, 2 H), 8.52 (m, 2 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-(4-pyridylmethyl)isothiourea (brown oil)

NMR ($CDCl_3$) δ: 2.30 (s, MeS), 2.87 (s, $MeNCH_2$, 3.27 (s, MeN =), 4.59 (s, CH_2), 7.18 (m, 2 H), 8.54 (m, 2 H)

(3) Title compound

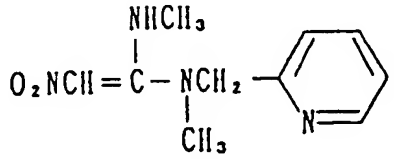
m.p.: 145-146 °C

NMR ($CDCl_3$) δ: 2.88 (s, $MeNCH_2$), 3.07 (d, J = 5 Hz, MeNH), 4.43 (s, CH_2), 6.54 (s, $=CHNO_2$), 7.21 (m, 2 H), 8.65 (m, 2 H), 9.78 (br, NH)

IR (Nujol): 1600, 1565, 1455, 1435, 1410, 1320, 1260 cm^{-1}

Example 44

1-Methylamino-1-[N-methyl-N-(2-pyridylmethyl)]amino-2-nitroethylene (Compound 63)



The steps (1), (2) and (3) of Example 37 were repeated except that N-methyl-N-(2-pyridylmethyl)amine was used in lieu of N-methyl-N-[2-(3-pyridyl)ethyl]amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(2-pyridylmethyl)thiourea (yellow brown viscous oil)

NMR ($CDCl_3$) δ: 3.15 (d, J = 5 Hz, MeNH), 3.31 (s, $MeNCH_2$), 4.90 (s, CH_2), 7.15-7.6 (m, 3 H, pyridine-H_2 & NH), 7.73 (t, J = 7 Hz, 8.55 (d, J = 5 Hz, 1 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-(2-pyridylmethyl)isothiourea (brown oil)

NMR ($CDCl_3$) δ: 2.30 (s, MeS), 2.91 (s, $MeNCH_2$), 3.28 (s, MeN=), 4.77 (s, CH_2), 7.05-7.45 (m, 2 H), 7.67 (m, 1 H), 8.56 (d, J = 5 Hz, 1 H)

(3) Title compound

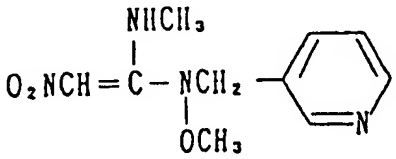
m.p.: 96-97 °C

NMR ($CDCl_3$) δ: 2.96 (s, $MeNCH_2$), 3.08 (d, J = 5 Hz, MeNH), 4.53 (s, CH_2), 6.57 (s, $=CHNO_2$, 7.30 (m, 2 H), 7.78 (m, 1 H), 8.63 (m, 1 H), 9.61 (br, NH)

IR (Nujol): 1580, 1545, 1425, 1380, 1280 cm^{-1}

Example 45

1-[N-methoxy-N-(3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene (Compound 64)



The steps (1), (2) and (3) of Example 37 were repeated except that O-methyl-N-(3-pyridylmethyl)-hydroxylamine was used in lieu of N-methyl-N-[2-(3-pyridyl)ethyl]amine to give the following compounds in the respective steps.

(1) N-Methoxy-N-(3-pyridylmethyl)-N'-methylthiourea (provide, however, that acetonitrile was used as the reaction solvent and the reaction was conducted at 50 °C for 5 hours)

m.p.: 95-96 °C

NMR ($CDCl_3$) δ: 3.15 (d, J = 5 Hz, 3 H), 3.63 (s, 3 H), 5.32 (s, 2H), 7.03-7.46 (br, NH), 7.27 (dd, J = 8 & 5 Hz, 1 H), 7.86 (dt, J = 8 & 2 Hz, 1 H), 8.56 (dd, J = 5 & 2 Hz, 1 H), 8.66 (d, J = 2 Hz, 1H)

(2) S-Methyl-N-methoxy-N-(3-pyridylmethyl)-N'-methylisothiourea (pale yellow oil)

NMR ($CDCl_3$) δ: 2.23 & 2.45 (each s, total 3 H), 3.26 & 3.32 (each s, total 3 H), 3.40 & 3.50 (each s, total 3 H), 4.08 & 4.52 (each s, total 2 H), 7.20-7.43 (m, 1 H), 7.76 (m, 1 H), 8.50-8.76 (m, 2 H)

(3) Title compound

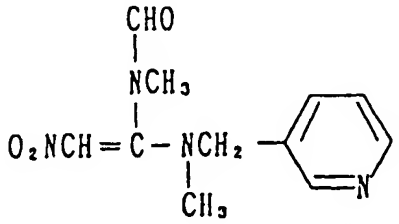
m.p. 100-101 °C

NMR ($CDCl_3$) δ: 3.18 (d, J = 5 Hz, 3 H), 3.45 (s, 3 H), 4.30 (s, 2 H), 6.90 (s, 1 H), 7.33 (dd, J = 8 & 5 Hz, 1 H), 7.73 (dt, J = 8 & 2 Hz, 1 H), 8.56-8.73 (m, 2 H), 9.73 (br, NH)

IR (Nujol): 1613, 1460, 1360, 1250, 1080 cm^{-1}

Example 46

1-(N-Formyl-N-methyl)amino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 65)



In 10 ml of dry THF was suspended 0.1 g of petroleum ether-washed 60% sodium hydride, followed by addition of 0.51 g (0.0023 mole) of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene. The mixture was stirred at room temperature overnight. Then, under ice-cooling, 0.6 g of formic acetic anhydride was added and the mixture was stirred at that temperature for 1 hour. The solvent was distilled off and the residue was diluted with 30 ml of water, neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (30 ml x 3). The extract was dried over $MgSO_4$, the CH_2Cl_2 was removed by distillation and the residue was subjected to silica gel column chromatography, elution being carried out with MeOH-$CHCl_3$ (1:5). The procedure gave 0.25 g of the title compound as pale yellow prisms.

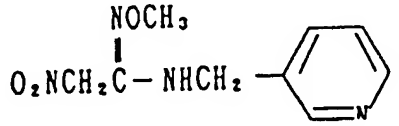
m.p.: 97-98 °C

NMR (DMSO-d_6) δ: 2.93 (s, 3 H), 3.03 (s, 3 H), 4.62 (br, 2 H), 6.86 (s, 1 H), 7.42 (dd, J = 8 & 5 Hz, 1 H), 7.73 (br d, J = 8 Hz, 1 H), 8.25 (s, 1 H), 8.55 (br, 2 H)

IR (Nujol): 1700, 1560, 1350, 1285, 1260, 890 cm^{-1}

Example 47

N^2-Methoxy-2-nitro-N^1-(3-pyridylmethyl)acetamidine (Compound 66)



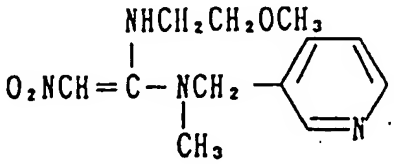
To 3 ml of isobutyl alcohol was added 0.75 g (0.0033 mole) of 1-methylthio-1-(3-pyridylmethyl)amino-2-nitroethylene,followed by addition of 0.56 g of O-methylhydroxylamine hydrochloride at 100-110 °C. Then, a solution of 0.93 ml of triethylamine in 1 ml of isobutyl alcohol was added dropwise at the same temperature with stirring over a period of 30 minutes. After completion of dropwise addition, the reaction mixture was allowed to cool to room temperature and the solvent was distilled off. The residue was purified by silica gel column chromatography [eluents: MeOH-$CHCl_3$ (1:3) in the first run and MeOH-$CHCl_3$ (1:10) in the second run] to give 0.23 g of the title compound as yellow crystals.

m.p.: 77-78 °C

NMR ($CDCl_3$) δ: 3.86 (s, 3 H), 4.37 (d, J = 6.3 Hz, 2 H), 5.04 (s, 2 H), 5.2-5.8 (br, 1 H), 7.32 (dd, J = 8.4 & 5.1 Hz, 1 H), 7.65 (dt, J = 8.4 & 1.5 Hz, 1 H), 8.4-8.8 (2 H, m)

Example 48

1-(2-Methoxyethyl)amino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene (Compound 67)



The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(3-pyridylmethyl)amine and (2-methoxy)ethyl isothiocyanate were used in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methyl isothiocyanate, respectively, to give the following compounds in the respective steps.

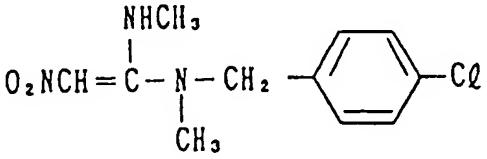
(1) N-(2-methoxyethyl)-N'-methyl-N'-(3-pyridylmethyl)-thiourea (colorless oil)
NMR ($CDCl_3$) δ: 3.06 (s, 3 H), 3.36 (s, 3 H), 3.57 (t, J = 5.1 Hz, 2 H), 3.91 (dt, J = 5.1 & 5.1 Hz, 2 H), 5.21 (s, 2 H), 5.9-6.3 (br, 1 H), 7.28 (dd, J = 8.4 & 5.1 Hz, 1 H), 7.75 (dt, J = 8.4 & 1.5 Hz, 1 H), 8.5-8.7 (m, 2 H)

2) S-Methyl-N-(2-methoxyethyl)-N'-methyl-N'-(3-pyridylmethyl)isothiourea (yellow oil)
NMR ($CDCl_3$) δ: 2.30 (s, 3 H), 2.88 (s, 3 H), 3.37 (s, 3 H), 3.4-3.8 (m, 4 H), 4.59 (s, 2 H), 7.25 (dd, J = 8.4 & 5.1 Hz, 1 H), 7.62 (dt, J = 8.4 & 1.5 Hz, 1 H), 8.4-8.7 (m, 2 H)

(3) Title compound
m.p. 55-57 °C
NMR ($CDCl_3$) δ: 2.79 (s, 3 H), 3.3-3.7 (m, 4 H), 3.41 (s, 3 H), 4.43 (s, 2 H), 6.53 (s, 1 H), 7.35 (dd, J = 8.4 & 1.5 Hz, 1 H), 7.60 (dt, J = 8.4 & 1.5 Hz, 1 H), 8.5-8.7 (m, 2 H), 9.4-9.9 (br, 1 H)

Example 49

1-[N-(4-Chlorobenzyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 68)



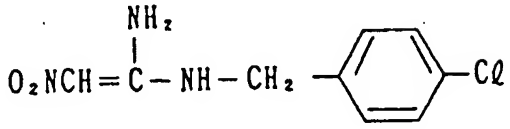
(1) In 50 ml of dry THF was dissolved 4.69 g (0.0205 mole) of N-(4-chlorobenzyl)-N-methyl-N'-methylthiourea, followed by addition of 0.82 g of 60% sodium hydride (oil). The mixture was refluxed for 1 hour. Then, under cooling with ice-water and stirring, 1.277 ml of methyl iodide was added dropwise and after completion of dropwise addition, the mixture was further stirred at room temperature for 45 minutes. The THF was distilled off and the residue was diluted with water (about 50 ml), saturated with sodium chloride, and extracted with AcOEt (100 ml x 3). The extract was dried over $MgSO_4$ and the solvent was distilled off to give 5.11 g of crude S-methyl-N-(4-chlorobenzyl)-N-methyl-N'-methylisothiourea as a colorless - pale yellow oil.
NMR ($CDCl_3$) δ: 2.28 (s, MeS), 2.80 (s, MeNCH$_2$), 3.26 (s, MeN=), 4.53 (s, CH_2), 7.14 & 7.31 (each d, J = 9 Hz, each 2 H)

(2) To 4.98 g (0.0205 mole) of S-methyl-N-(4-chlorobenzyl)-N-methyl-N'-methylisothiourea prepared in (1) was added 25 ml of nitromethane and the mixture was refluxed for 6.5 hours. The nitromethane was distilled off and the residue was subjected to silica gel (240 g) column chromatography using MeOH-$CHCl_3$ (1:10) as an eluent to give 5.23 g of an orange-colored oil. To this oil were added small amounts of EtOH and ether and the mixture was cooled in a dry ice-acetone bath and triturated to give crystals. After addition of ether, the crystals were collected by filtration, washed with ether and dried. The procedure gave 3.69 g of the title compound as pale yellow cyrstals.
m.p.: 98-99 °C
NMR ($CDCl_3$) δ: 2.79 (s, MeNCH$_2$), 3.05 (d, J = 5 Hz, MeNH), 4.34 (s, CH_2), 6.53 (s, =$CHNO_2$), 7.17

& 7.38 (each d, J = 8 Hz, each 2 H), 9.79 (br, NH)
IR (Nujol): 1450, 1310, 1235, 1070, 1025 cm^{-1}

Example 50

1-Amino-1-(4-chlorobenzyl)amino-2-nitroethylene (Compound 69)



To 2.59 g (0.01 mole) of 1-(4-chlorobenzyl)amino-1-methylthio-2-nitroethylene were added 45 ml of EtOH, 10 ml of THF and 1.02 g of 25% aqueous ammonia and the mixture was stirred at an external temperature of 60 °C for 5.5 hours. During this period, 1.02 g each of 25% aqueous ammonia was added after 1, 2 and 3 hours of reaction. The reaction mixture was ice-cooled and stirred, whereupon crystals separated out. The crystals were collected by filtration, washed with EtOH and ether in that order, and dried. The procedure gave 1.11 g of the title compound as white crystals.

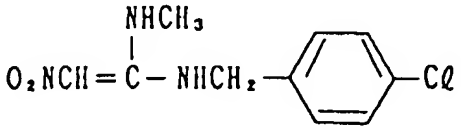
m.p.: 215-216 °C (decompn.)

NMR (DMSO-d_6) δ: 4.47 (d, J = 7 Hz, CH_2), 6.45 (s, $=CHNO_2$), 7.34 & 7.44 (each d, J = 9 Hz, each 2 H), 8.02 (br, NH_2), 9.25 (br, NH)

IR (Nujol): 3100, 1560, 1430, 1405, 1195, 1030 cm^{-1}

Example 51

1-(4-Chlorobenzyl)amino-1-methylamino-2-nitroethylene (Compound 70)



In 100 ml of EtOH on reflux was dissolved 2.59 g (0.01 mole) of 1-(4-chlorobenzyl)amino-1-methylthio-2-nitroethylene, and with refluxing continued, a solution of 1.94 g of 40% aqueous methylamine solution in 10 ml of EtOH was added dropwize over a period of 50 minutes. After completion of dropwise addition, the mixture was further refluxed for 15 minutes, at the end of which time it was cooled with ice-water, whereupon crystals separated out. The crystals were collected by filtration, washed with EtOH and ether in that order, and dried. The procedure gave 1.66 g of the title compound as white crystals.

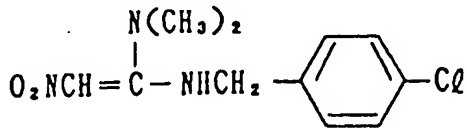
m.p.: 219-220 °C (decompn.)

NMR (DMSO-d_6) δ: 2.88 (br d, J = 3 Hz, Me), 4.43 (d, J = 6 Hz, CH_2), 6.43 (s, $=CHNO_2$), 7.40 (s, 4 H), 7.7 (br, MeNH), 9.9 (br, $HNCH_2$)

IR (Nujol): 1455, 1425, 1375, 1360, 1215, 995 cm^{-1}

Example 52

1-(4-Chlorobenzyl)amino-1-dimethylamino-2-nitroethylene (Compound 71)



In 100 ml of EtOH was dissolved 2.59 g (0.01 mole) of 1-(4-chlorobenzyl)amino-1-methylthio-2-nitroethylene with heating. Then, with refluxing and stirring, a solution of 2.25 g of 50% aqueous dimethylamine solution in 10 ml of EtOH was added dropwise over a period of 35 minutes. After completion

of dropwise addition, the mixture was further stirred and refluxed for 2.5 hours. The solvent was then distilled off and the residue was diluted with ether and triturated, whereupon crystals separated. After addition of EtOH and ether (about 1:5), the crystals were collected by filtration, washed with ether and dried. The procedure gave 1.21 g of the title compound as white crystals.

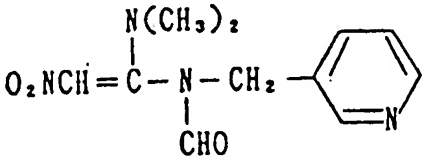
m.p.: 133-135 °C

NMR ($CDCl_3$) δ: 2.91 (s, Me_2N), 4.45 (d, J = 6 Hz, CH_2), 6.51 (s, $=CHNO_2$), 7.30 (s, 4 H), 9.79 (br, NH)

IR (Nujol): 1620, 1500, 1435, 1420, 1370, 1220, 1195 cm^{-1}

Example 53

1-Dimethylamino-1-[N-formyl-N-(3-pyridylmethyl)]-amino-2-nitroethylene (Compound 72)



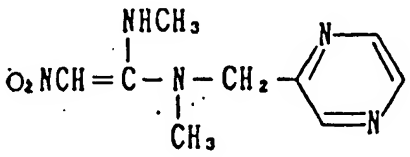
In 10 ml of dry THF was suspended 0.1 g of 60% sodium hydride (oil) followed by addition of 0.56 g (0.0025 mole) of 1-dimethylamino-1-(3-pyridylmethyl)-amino-2-nitroethylene, and the mixture was stirred at room temperature overnight. Then, under ice-cooling, 0.7 g of formic acetic anhydride was added, followed by stirring at the same temperature for 2 hours. The solvent was distilled off and the residue was diluted with 30 ml of water, neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (30 ml x 3). The extract was dried over $MgSO_4$, the solvent was distilled off and the residue was subjected to silica gel column chromatography using MeOH-$CHCl_3$ (1:5) as an eluent. The procedure gave 0.2 g of the title compound as a pale yellow viscous oil.

NMR (DMSO-d_6) δ: 2.90 (s, 6 H), 4.40-5.06 (m, 2 H), 6.73 (s, 1 H), 7.33 (dd, J = 8 & 5 Hz, 1 H), 7.75 (br d, J = 8 Hz, 1 H), 8.26 (s, 1 H), 8.55 (br, 2 H)

IR (neat): 1685, 1570, 1500, 1350, 1270 cm^{-1}

Example 54

1-Methylamino-1-[N-methyl-N-(2-pyrazinyl)methyl]amino-2-nitroethylene (Compound 73)



The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(2-pyrazyl)methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-[(2-pyrazyl)methyl]thiourea

m.p.: 123-124 °C

NMR ($CDCl_3$) δ: 3.17 (d, J = 5 Hz, 3 H), 3.26 (s, 2 H), 5.12 (s, 2 H), 6.42 (br, 1 H), 8.53 (s, 2 H), 8.72 (s, 1 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-[(2-pyrazyl)methyl]isothiourea (pale yellow oil)

NMR ($CDCl_3$) δ: 2.32 (s, 3 H), 2.98 (s, 3 H), 3.26 (s, 3 H), 4.76 (s, 2 H), 8.45-8.66 (m, 3 H)

(3) Title compound

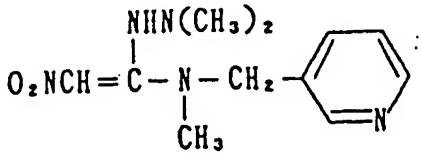
m.p.: 132-133 °C

NMR ($CDCl_3$) δ: 2.93 (s, 3 H), 3.09 (d, J = 5 Hz, 3 H), 4.56 (s, 2 H), 6.60 (s, 1 H), 8.62 (s, 3 H), 9.60 (br, 1 H)

IR (Nujol): 3150, 1580, 1410, 1280, 1240, 1020, 990 cm^{-1}

Example 55

1-(2,2-Dimethyl-1-hydrazino)-1-[N-methyl-N-(3-pyridylmethyl]amino-2-nitroethylene (Compound 74)



A mixture of 4.3 g (0.024 mole) of 1-(2,2-dimethyl-1-hydrazino)-1-methylthio-2-nitroethylene and 3.6 g of N-methyl-N-(3-pyridylmethyl)amine was stirred at 90-100 °C for 4 hours, after which it was subjected to silica gel column chromatography using MeOH-$CHCl_3$ (1:10) as an eluent. The resulting crystals were washed with ether and dried to give 0.7 g of the title compound. NMR of this product showed that it was a 3:2 mixture of the title compound and N^2-dimethylamino-N^1-methyl-2-nitro-N^1-(3-pyridylmethyl)acetamidine.

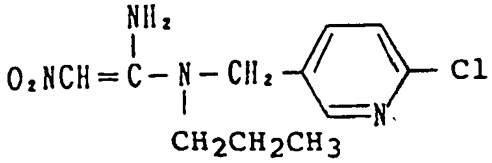
m.p.: 80-82 °C

NMR ($CDCl_3$) δ: 2.40 (s, 2.4 H), 2.59 (s, 3.6 H), 2.87 (s, 1.2 H), 2.90 (s, 1.8 H), 4.61 (s, 0.8 H), 4.63 (s, 1.2 H), 6.00 (s, 0.8 H), 6.47 (s, 0.6 H), 7.15-7.45 (m, 1 H), 7.45-7.80 (m, 1 H), 8.45-8.70 (m, 2 H), 10.1-10.5 (br s, 0.6 H)

IR (Nujol): 3130, 1585, 1570, 1445, 1425 cm^{-1}

Example 56

1-Amino-1-[N-(6-chloro-3-pyridylmethyl)-N-n-propyl]-amino-2-nitroethylene (Compound 75)



In 40 ml of EtOH was dissolved 2.83 g (0.0094 mole) of 1-[N-(6-chloro-3-pyridylmethyl)-N-n-propyl]-amino-1-methylthio-2-nitroethylene followed by addition of 0.96 ml of 25% aqueous ammonia. The mixture was stirred at room temperature for 3 hours. The resulting crystals were collected by filtration, washed with small amounts of EtOH and ether in that order, and dried to give 1.35 g of the title compound as pale yellow crystals.

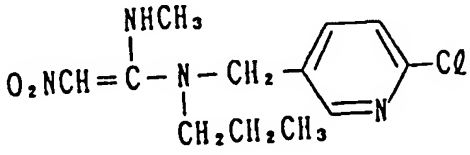
m.p: 185-186 °C (decompn.)

NMR (DMSO-d_6) δ: 0.87 (t, J = 7 Hz, CH_2CH_3), 1.59 (sextet, J = 7 Hz, CH_2CH_3), 3.31 (t, J = 7 Hz, NCH_2CH_2), 4.68 (s, CH_2-pyridine), 6.59 (s, $=CHNO_2$), 7.50 (d, J = 8 Hz, 1 H), 7.71 (dd, J = 8 & 2 Hz, 1 H), 8.31 (d, J = 2 Hz, 1 H), 8.99 (br, NH_2)

IR (Nujol): 1615, 1550, 1455, 1335, 1320, 1300, 1285 cm^{-1}

Example 57

1-[N-(6-Chloro-3-pyridylmethyl)-N-n-propyl]amino-1-methylamino-2-nitroethylene (Compound 76)

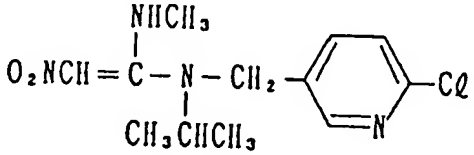


The steps (1), (2) and (3) of Example 13 were repeated except that N-(6-chloro-3-pyridylmethyl)-N-n-propylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N-n-propyl-N'-methylthiourea (pale yellow crystals)
m.p.: 95-96 °C
NMR ($CDCl_3$) δ: 0.89 (t, J = 8 Hz, CH_2CH_3), 1.63 (sextet, J = 8 Hz, CH_2CH_3), 3.17 (d, J = 5 Hz, MeN), 3.36 (t, J = 8 Hz, CH_2CH_2N), 5.16 (s, CH_2-pyridine), 5.87 (br q, J = 5 Hz, NH), 7.30 (d, J = 8 Hz, 1 H), 7.78 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H)
(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N-n-propyl-N'-methylisothiourea (yellow oil)
(provided, however, that after addition of 60% sodium hydride (oil), the mixture was stirred at 50 °C for 1 hour.)
NMR ($CDCl_3$) δ: 0.85 (t, J = 7 Hz, CH_2CH_3),1.55 (sextet, J = 7 Hz, CH_2CH_3), 2.26 (s, MeS), 3.21 (s, MeN=), 3.29 (t, J = 7 Hz, CH_2CH_2N), 4.52 (s, CH_2-pyridine), 7.26 (d, J = 8 Hz, 1 H), 7.60 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H)
(3) Title compound (pale yellow - pale brown crystals) (provided, however, that the reaction mixture was refluxed in nitromethane for 34 hours.)
m.p.: 102-103 °C
NMR ($CDCl_3$) δ: 0.88 (t, J = 7 Hz, CH_2CH_3), 1.63 (sextet, J = 7 Hz, CH_2CH_3), 3.04 (t, J = 7 Hz, CH_2CH_2N), 3.08 (d, J = 5 Hz, MeN), 4.40 (s, CH_2-pyridine), 6.54 (s, $=CHNO_2$), 7.38 (d, J = 8 Hz, 1 H), 7.60 (dd, J = 8 & 2 Hz, 1 H), 8.33 (dd, J = 2 Hz, 1 H), 9.78 (br q, J = 5 Hz, NH)
IR (Nujol): 1590, 1520, 1450, 1350, 1270, 1245, 1095 cm^{-1}

Example 58

1-[N-(6-Chloro-3-pyridylmethyl)-N-i-propyl]amino-1-methylamino-2-nitroethylene (Compound 77)



The steps (1), (2) and (3) of Example 13 were repeated except that N-(6-chloro-3-pyridylmethyl)-N-i-propylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N-i-propyl-N'-methylthiourea (pale yellow crystals)
m.p.: 92-93 °C
NMR ($CDCl_3$) δ: 1.17 (d, J = 7 Hz, Me_2CH), 3.12 (d, J = 5 Hz, MeN), 4.87 (s, CH_2), 5.08 (septet, J = 7 Hz, Me_2CH), 5.80 (br q, J = 5 Hz, NH), 7.30 (d, J = 8 Hz, 1 H), 7.65 (dd, J = 8 & 2 Hz, 1 H), 8.27 (d, J = 2 Hz, 1 H)
(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N-i-propyl-N'-methylisothiourea (pale brown oil)
(provided, however, that after addition of 60% sodium hydride (oil), the mixture was stirred at 50 °C for 1 hour.)
NMR ($CDCl_3$) δ: 1.20 (d, J-7 Hz, Me_2CH), 2.23 (s, MeS), 3.10 (s, MeN=), 4.24 (s, CH_2-pyridine), 4.44 (septet, J = 7 Hz, Me_2CH), 7.23 (d, J = 8 Hz, 1 H), 7.56 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H)
(3) Title compound (white - pale brown crystals)
(provided, however, that the reaction mixture was refluxed in nitromethane for 130 hours.)
m.p.: 119-120 °C
NMR ($CDCl_3$) δ: 1.31 (d, J = 7 Hz, Me_2CH), 3.04 (d, J = 5 Hz, MeN), 3.79 (septet, J = 7 Hz, Me_2CH), 4.20 (s, CH_2), 6.56 (s, $=CHNO_2$), 7.30 (d, J = 8 Hz, 1 H), 7.56 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H), 9.78 (br q, J = 5 Hz, NH)
IR (Nujol): 1590, 1450, 1360, 1335, 1270, 1235, 1105 cm^{-1}

Example 59

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 78)

(1) In 50 ml of acetonitrile, 4.0 g (0.028 mole) of 2-chloro-5-methylaminopyridine and 3.7 g of methyl isothiocyanate were refluxed for 52.5 hours and the reaction mixtrue was concentrated. To the residue were added 30 ml of ice-water and 2 ml of 3N-HCl, followed by extraction with AcOEt (50 ml x 3). The extracts were pooled, washed successively with 3N-HCl (4 times), aqueous sodium chloride solution (4 times) and aqueous sodium hydrogen carbonate solution (once), and dried over $MgSO_4$. The AcOEt was distilled off under reduced pressure and after addition of ether, the crystals were collected by filtration and dired to give 2.8 g of N-(6-chloro-3-pyridyl)-N-methyl-N'-methylthiourea as white crystals.

m.p.: 87.5-88 °C

NMR ($CDCl_3$) δ: 3.09 (d, J = 4.5 Hz, 3 H), 3.65 (s, 3 H), 5.3-6.0 (m, 1 H), 7.47 (d, J = 8.4 Hz, 1 H), 7.61 (dd, J = 8.4 & 2.4 Hz, 1 H), 8.33 (d, J = 2.4 Hz, 1 H)

(2) In 10 ml of dry tetrahydrofuran was suspended 0.9 g of 60% sodium hydride (oil) which had been washed twice with petroleum ether, and with stirring, a solution of 2.5 g (0.012 mole) of N-(6-chloro-3-pyridyl)-N-methyl-N'-methylthiourea in 30 ml of dry tetrahydrofuran was added dropwise. After completion of dropwise addition, the mixture was stirred at 50 °C for 0.5 hour. Then, at room temperature, 2.2 g of methyl iodide was added dopwise and the mixture was further stirred for 3 hours. The reaction mixture was concentrated under reduced pressure and after addition of 50 ml of iced water and 3 ml of 3N-HCl, the concentrate was extracted with AcOEt (50 ml x 3). The extracts were pooled, washed with water (twice) and dried over $MgSO_4$. Finally, the AcOEt was distilled off under reduced pressure to recover 2.6 g of crude S-methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-methylisothiourea as a brown oil.

NMR ($CDCl_3$) δ: 2.07 & 2.38 (each s, 3 H), 3.06 & 3.27 (each s, 3 H), 3.17 & 3.30 (each s, 3 H), 6.9-7.6 (m, 2 H), 7.90 & 8.24 (each d, J = 3.0 Hz, 1 H)

(3) In 40 ml of nitromethane, 2.6 g (0.011 mole) of S-methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-methylisothiourea was refluxed for 63 hours. The reaction mixture was then concentrated and the residue was subjected to silica gel column chromatography using hexane-acetone (1:2) as an eluent. The resulting crystals were washed with ether and dried to give 1.3 g of the title compound as pale yellow crystals.

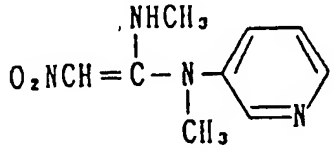
m.p.: 108-109 °C

NMR ($CDCl_3$) δ: 2.75 (d, J = 5.1 Hz, 3 H), 3.30 (s, 3 H), 6.63 (s, 1 H), 7.2-7.6 (m, 2 H), 8.2-8.3 (m, 1 H), 9.6-10.3 (m, 1 H)

IR (Nujol): 3120, 1600 cm^{-1}

Example 60

1-Methylamino-1-[N-methyl-N-(3-pyridyl)]amino-2-nitroethylene (Compound 79)

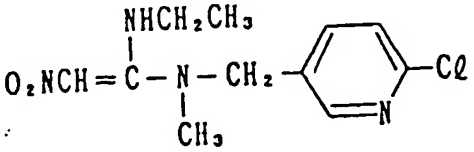


The steps (1), (2) and (3) of Example 59 were repeated except that 3-methylaminopyridine was used in lieu of 2-chloro-5-methylaminopyridine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(3-pyridyl)thiourea (white crystals)
m.p.: 93-94 °C
NMR ($CDCl_3$) δ: 3.08 (d, J = 4.5 Hz, 3 H), 3.69 (s, 3 H), 5.2-5.8 (m, 1 H), 7.47 (dd, J = 8.1 & 4.7 Hz, 1 H), 7.64 (dt, J = 8.4 & 2.3 Hz, 1 H), 8.4-8.8 (m, 2 H)
(2) S-Methyl-N-methyl-N'-methyl-N'-(3-pyridyl)isothiourea (red brown oil)
NMR ($CDCl_3$) δ: 2.01 & 2.37 (each s, 3 H), 3.05 & 3.27 (each s, 3 H), 3.17 & 3.29 (each s, 3 H), 6.9-7.6 (m, 2 H), 8.0-8.6 (m, 2H)
(3) Title compound (pale brown crystals)
m.p.: 113-114 °C
NMR ($DMSO-d_6$) δ: 2.66 (d, J = 5.1 Hz, 3 H), 3.29 (s, 3 H), 6.53 (s, 1 H), 7.41 (dd, J = 8.4 & 4.5 Hz, 1 H), 7.5-7.8 (m, 1 H), 8.2-8.7 (m, 2 H), 9.4-10.0 (m, 1 H)
IR (Nujol): 3190, 3140, 1595 cm^{-1}

Example 61

1-[N-(6-Chloro-3-pyridylmethyl)-N-methyl]amino-1-ethylamino-2-nitroethylene (Compound 80)

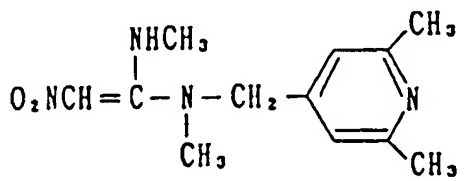


Using N-(6-chloro-3-pyridylmethyl)-N-methylamine and ethyl isothiocyanate in lieu of N-ethyl-N-(3-pyridylmethyl)amine and methylisothiocyanate, respectively, the reaction steps (1), (2) and (3) of Example 13 were followed to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N'-ethyl-N-methylthiourea (white crystals)
m.p. 82-83 °C
NMR ($CDCl_3$) δ: 1.24 (t, J = 7 Hz, CH_2CH_3), 3.04 (s, MeN), 3.72 (dq, J = 5 & 7 Hz, CH_2CH_3), 5.22 (s, CH_2-pyridine), 5.66 (br, NH), 7.33 (d, J = 8 Hz, 1H), 7.79 (dd, J = 8 & 2 Hz, 1H), 8.33 (d, J = 2 Hz, 1 H)
(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N'-ethyl-N-methylisothiourea (brown oil)
NMR ($CDCl_3$) δ: 1.12 (t, J = 7 Hz, CH_2CH_3), 2.30 (s, MeS), 2.87 (s, $MeNCH_2$), 3.51 (q, J = 7 Hz, CH_2CH_3), 4.52 (s, CH_2-pyridine), 7.30 (d, J = 8 Hz, 1 H), 7.62 (dd, J = 8 & 2 Hz, 1 H), 8.33 (d, J = 2 Hz, 1 H)
(3) Title compound (white - pale yellow crystals)
m.p.: 132-133 °C
NMR ($CDCl_3$) δ: 1.33 (t, J = 7 Hz, CH_2CH_3), 2.80 (s, MeN), 3.38 (dq, J = 5 & 7 Hz, CH_2CH_3), 4.40 (s, CH_2-pyridine), 6.49 (s, $=CHNO_2$), 7.38 (d, J = 8 Hz, 1 H), 7.59 (dd, J = 8 & 2 Hz, 1 H), 8.30 (d, J = 2 Hz, 1 H), 9.51 (br t, J = 5 Hz, NH)
IR (Nujol): 1600, 1535, 1445, 1305, 1290 cm^{-1}

Example 62

1-[N-(2,6-Dimethyl-4-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 81)



The steps (1), (2) and (3) of Example 13 were repeated except that N-(2,6-dimethyl-4-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

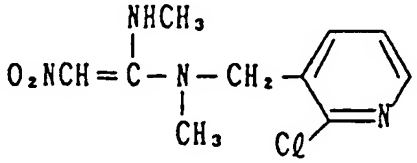
(1) N-(2,6-dimethyl-4-pyridylmethyl)-N-methyl-N'-methylthiourea (white crystals)
m.p.: 207-208 °C
NMR ($CDCl_3$) δ: 2.49 (s, pyridine-Me x 2), 3.09 (s, $MeNCH_2$), 3.18 (d, J = 5 Hz, MeNH), 5.10 (s, CH_2-pyridine), 5.91 (br q, J = 5 Hz, NH), 6.86 (s, pyridine-H_2)

(2) S-Methyl-N-(2,6-dimethyl-4-pyridylmethyl)-N-methyl-N'-methylisothiourea (brown oil)
(provide, however, that after addition of 60% sodium hydride (oil), the mixtrue was stirred at 50 °C for 1 hour and at reflux temperature for 1 hours.)
NMR ($CDCl_3$) δ: 2.30 (s, MeS), 2.50 (s, pyridien-Me x 2), 2.86 (s, MeNH), 3.27 (s, MeN=), 4.53 (s, pyridine-CH_2), 6.84 (s, pyridine-H_2)

(3) Title compound (white crystals)
m.p.: 131-133 °C
NMR ($CDCl_3$) δ: 2.53 (s, pyridine-Me x 2), 2.87 (s, $MeNCH_2$), 3.05 (d, J = 5 Hz, MeNH), 4.34 (s, CH_2), 6.54 (s, $=CHNO_2$), 6.83 (s, pyridine-H_2)
IR (Nujol): 1570, 1460, 1395, 1310, 1230 cm^{-1}

Example 63

1-[N-(2-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 82)



The steps (1), (2) and (3) of Example 13 were repeated except that N-(2-chloro-3-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

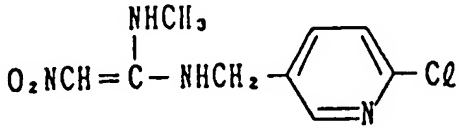
(1) N-(2-chloro-3-pyridylmethyl)-N-methyl-N'-methylthiourea (white crystals)
m.p.: 143-144 °C
NMR ($CDCl_3$) δ: 3.17 (s, $MeNCH_2$), 3.18 (d, J = 5 Hz, MeNH), 5.29 (s, CH_2), 5.98 (br q, J = 5 Hz, NH), 7.26 (dd, J = 8 & 5 Hz, 1 H), 7.66 (d, J = 8 & 1 Hz, 1 H), 8.31 (dd, J = 5 & 1 Hz, 1 H)

(2) S-Methyl-N-(2-chloro-3-pyridylmethyl)-N-methyl-N'-methylisothiourea (pale yellow oil)
(provided, however, that after addition of 60% sodium hydride (oil), the mixture was stirred at 50 °C for 1 hour.)
NMR ($CDCl_3$) δ: 2.29 (s, MeS), 2.95 (s, $MeNCH_2$), 3.26 (s, MeN=), 4.67 (s, CH_2-pyridine), 7.24 (dd, J = 8 & 5 Hz, 1 H), 7.62 (dd, J = 8 & 1 Hz, 1 H), 8.32 (dd, J = 5 & 1 Hz, 1 H)

(3) Title compound (pale yellow crystals)
(provided, however, that the reaction mixture was refluxed in nitromethane for 2.25 hours)
As determined by NMR, the purity of this product was found to be about 75%.
m.p.: 106-113 °C
NMR ($CDCl_3$) δ: (for the title compound only) 2.90 (s, $MeNCH_2$), 3.04 (d, J = 5 Hz, MeNH), 4.50 (s, CH_2), 6.54 (s, $=CHNO_2$), 7.37 (dd, J = 8 & 5 Hz), 7.68 (dd, J = 8 & 1 Hz), 8.43 (dd, J = 5 & 1 Hz), 9.78 (br q, J = 5 Hz, NH)
IR (Nujol): 1560, 1450, 1405, 1310, 1260 cm^{-1}

Example 64

1-(6-Chloro-3-pyridylmethyl)amino-1-methylamino-1-methylamino-2-nitroethylene (Compound 28)

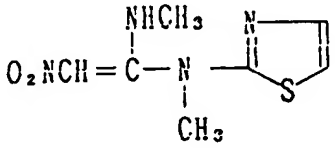


The steps (1), (2) and (3) of Example 8 were repeated except that 6-chloro-3-pyridylmethylamine was used in lieu of N-methyl-N-3-pyridylmethylamine to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridylmethyl)-N'-methylthiourea (white crystals)
m.p.: 133-134 °C
NMR ($CDCl_3$) δ: 3.01 (d, J = 5 Hz, Me), 4.80 (d, J = 6 Hz, CH_2), 7.25 (br, $NHCH_3$), 7.32 (d, J = 8 Hz, 1 H), 7.66 (br t, J = 6 Hz, $NHCH_2$), 7.78 (dd, J = 8 & 2 Hz, 1H), 8.37 (d, J = 2 Hz, 1 H)
(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N'-methylisothiourea (oil)
NMR ($CDCl_3$) δ: 2.39 (s, MeS), 2.93 (s, MeN), 4.22 (br, NH), 4.50 (s, CH_2), 7.27 (d, J = 8 Hz, 1 H), 7.69 (dd, J = 8 & 2 Hz, 1 H), 8.39 (d, J = 2 Hz, 1 H)
(3) Title compound (white - pale yellow crystals)
This product was found to be in agreement with Compound 28 according to Example 10 in melting point, NMR, IR and TLC Rf.

Example 65

1-Methylamino-1-[N-methyl-N-(2-thiazolyl)]amino-2-nitroethylene (Compound 83)

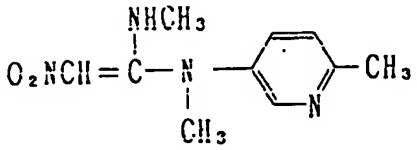


The steps (1), (2) and (3) of Example 59 were repeated except that 2-methylaminothiazole was used in lieu of 2-chloro-5-methylaminopyridine to obtain the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(2-thiazolyl)thiourea (white crystals)
(provided that the reaction mixture was refluxed in toluene for 8 hours and the product was purified by silica gel column chromatography)
m.p.: 68-69 °C
NMR ($CDCl_3$) δ: 3.24 (d, J = 4 Hz, 3 H), 3.95 (s, 3 H), 6.69 (d, J = 4 H, 1 H), 7.42 (d, J = 4 Hz, 1 H), 11.95 (br, 1 H)
(2) S-Methyl-N-methyl-N'-methyl-N'-(2-thiazolyl)isothiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 2.33 (s, 3 H), 3.41 (s, 3 H), 3.75 (s, 3 H), 6.74 (d, J = 4 Hz, 1 H), 7.40 (d, J = 4 Hz, 1 H)
(3) Title compound (pale yellow crystals)
(provided that the reaction was conducted for 25 hours and the product was concentrated to give crystals)
m.p.: 155-156 °C
NMR ($CDCl_3$): 2.98 (d, J = 5 Hz, 3 H), 3.42 (s, 3 H), 6.71 (s, 3 H), 6.91 (d, J = 4 Hz, 1 H), 7.36 (d, J = 4 Hz, 1 H), 9.87 (br, 1 H)
IR (Nujol): 3050, 1610, 1500, 1400, 1320, 1260, 1100, 1010 cm^{-1}

Example 66

1-Methylamino-1-[N-methyl-N-(6-methyl-3-pyridyl)]-amino-2-nitroethylene (Compound 84)



(1) In a solution of 1.9 g NaOH in 30 ml water was dissolved 4.3 g (0.02 mole) of 2-methyl-5-methylamino-pyridine oxalate and the solution was extracted with AcOEt (50 ml, 30 ml x 2). The AcOEt layers were combined, washed with water and dried over $MgSO_4$. After concentration, 30 ml of toluene and 1.8 g of methyl isothiocyanate were added to the concentrate and the mixture was refluxed for 8 hours. Then, 0.8 g of methyl isothiocyanate was further added and the mixture was refluxed for 7.5 hours. The reaction mixture was cooled to -20 °C and the resulting crystals were collected by filtration, washed with cold toluene and dried. The procedure gave 2.2 g of N-methyl-N'-methyl-N'-(6-methyl-3-pyridyl)thiourea as white crystals.

m.p.: 134-135 °C

NMR ($CDCl_3$) δ: 2.62 (3 H, s), 3.06 (3 H, d, J = 4.2 Hz), 3.66 (3 H, s), 5.2-5.9 (1 H, m, NH), 7.30 (1 H, d, J = 8.4 Hz), 7.49 (1 H, dd, J = 8.4 & 2.7 Hz), 8.42 (1 H, d, J = 2.7 Hz)

(2) The reaction procedure of Example 59 (2) was repeated except that N-methyl-N'-methyl-N'-(6-methyl-3-pyridyl)thiourea was used in lieu of N-(6-chloro-3-pyridyl)-N-methyl-N'-methylthiourea to give S-methyl-N-methyl-N'-methyl-N'-(6-methyl-3-pyridyl)isothiourea as oil.

NMR ($CDCl_3$) δ: 2.01 & 2.37 (3 H, each s), 2.49 & 2.53 (3 H, each s), 3.04 & 3.17 & 3.24 & 3.30 (6 H, each s), 6.9-7.6 (2 H, m), 8.0-8.5 (1 H, m)

(3) The reaction procedure of Example 59 (3) was repeated except that S-methyl-N-methyl-N'-methyl-N'-(6-methyl-3-pyridyl)isothiourea was used in lieu of S-methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-methylisothiourea and that the reaction was conducted for 23 hours. The procedure gave the title compound as yellow-brown crystals.

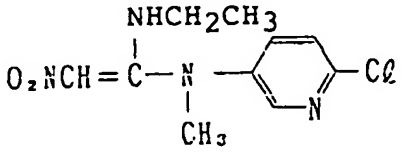
m.p.: 120-121 °C

NMR ($CDCl_3$) δ: 2.57 (3 H, s), 2.65 (3 H, d, J = 5.4 Hz), 3.30 (3 H, s), 6.67 (1 H, s), 7.23 (1 H, d, J = 8.7 Hz), 7.39 (1 H, dd, J = 8.4 & 2.7 Hz), 8.38 (1 H, d, J = 2.7 Hz), 9.7-10.4 (1 H, m, NH)

IR (Nujol): 3110, 1600 cm^{-1}

Example 67

1-[N-(6-chloro-3-pyridyl)-N-methyl]amino-1-ethylamino-2-nitroethylene (Compound 85)



The steps (1), (2) and (3) of Example 59 were repeated except that ethyl isothiocyanate was used in lieu of methylisothiocyanate to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridyl)-N-methyl-N'-ethylthiourea (yellow oil)

(provided that the reaction mixture was refluxed in toluene for 78 hours and the product was purified by silica gel column chromatography)

NMR ($CDCl_3$) δ: 1.13 (3 H, t, J = 6.6 Hz), 3.4-3.9 (2 H, m), 3.63 (3 H, s), 5.0-5.8 (1 H, br), 7.46 (1 H, d, J = 8.4 Hz), 7.61 (1 H, dd, J = 8.4 & 2.7 Hz), 8.33 (1 H, d, J = 2.7 Hz)

(2) S-Methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-ethylisothiourea (yellow oil)

NMR ($CDCl_3$) δ: [main component • • • 76%] 1.23 (3 H, t, J = 7.2 Hz), 2.04 (3 H, s), 3.28 (3 H, s), 3.53

(2 H, q, J = 7.2 Hz), 6.9-7.6 (2 H, m), 8.22 (1 H, d, J = 2.7 Hz) [a small amount of isomer• • •24%], 2.73 (3 H, s), 3.13 (3 H, s), 3.1-3.4 (2 H, m), 7.89 (1 H, d, J = 2.7 Hz)

(3) Title compound (pale yellow crystals)

(provided that the reaction was conducted for 64 hours and the reaction mixture was concentrated to give crystals)

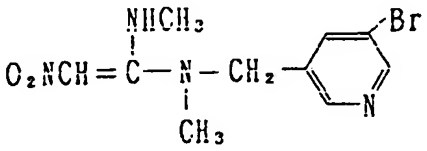
m.p.: 118-119 • C

NMR ($CDCl_3$) δ: 1.19 (3 H, t, J = 7.5 Hz), 3.00 (2 H, dt, J = 7.5 & 6.3 Hz), 3.29 (3 H, s), 6.61 (1 H, s), 7.3-7.6 (2 H, m), 8.1-8.4 (1 H, m)

IR (Nujol): 3200, 1605, 1375, 1300 cm^{-1}

Example 68

1-[N-(5-Bromo-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 86)



The steps (1), (2) and (3) of Example 13 were repeated except that crude N-(5-bromo-3-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(5-Bromo-3-pyridylmethyl)-N-methyl-N'-methylthiourea (pale yellow oil)

(provided that the product was purified by silica gel column chromatography)

NMR ($CDCl_3$) δ: 3.05 (s, $MeNCH_2$), 3.19 (d, J = 5 Hz, MeNH), 5.24 (s, CH_2), 5.88 (br q, J = 5 Hz, NH), 7.91 (m, 1 H), 8.47 (d, J = 2 Hz, 1 H), 8.62 (d, J = 2 Hz, 1 H)

(2) S-Methyl-N-(5-bromo-3-pyridylmethyl)-N-methyl-N'-methylisothiourea (oil)

NMR ($CDCl_3$) δ: 2,31 (s, MeS), 2.88 (s, $MeNCH_2$), 3.26 (s, MeN =), 4.56 (s, CH_2), 7.77 (m, 1 H), 8.47 (d, J = 2 Hz, 1 H), 8.60 (d, J = 2 Hz, 1 H)

(3) Title compound (pale yellowish brown crystals)

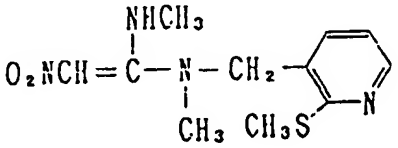
m.p.: 116-117 • C

NMR ($CDCl_3$) δ: 2.84 (s, $MeNCH_2$), 3.08 (d, J = 5 Hz, MeNH), 4.42 (s, CH_2), 6.54 (s, $=CHNO_2$), 7.76 (m, 1 H), 8.48 (d, J = 2 Hz, 1H), 8.68 (d, J = 2 Hz, 1 H), 9.72 (br q, J = 5 Hz, NH)

IR (Nujol): 1595, 1465, 1425, 1405, 1260 cm^{-1}

Example 69

1-Methylamino-1-[N-methyl-N-(2-methylthio-3-pyridylmethyl)]amino-2-nitroethylene (Compound 87)



The steps (1), (2) and (3) of Example 13 were repeated except that N-(2-methylthio-3-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(2-methylthio-3-pyridylmethyl)-thiourea (white - pale yellow crystals)

m.p.: 105-106 • C

NMR ($CDCl_3$) δ: 2.61 (s, MeS), 3.15 (d, J = 5 Hz, MeNH), 3.17 (s, $MeNCH_2$), 5.00 (s, CH_2), 5.77 (br, NH), 7.01 (dd, J = 8 & 5 Hz, 1 H), 7.36 (dd, J = 8 & 1 Hz, 1 H), 8.40 (dd, J = 5 & 1 Hz, 1 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-(2-methylthio-3-pyridylmethyl)isothiourea (yellow oil)

NMR ($CDCl_3$) δ: 2.28 (s, MeS), 2.59 (s, pyridine-SMe), 2.89 (s, $MeNCH_2$), 3.27 (s, MeN =), 4.53 (s,

CH_2), 6.98 (dd, J = 8 & 5 Hz, 1 H), 7.40 (dd, J = 8 & 1 Hz, 1 H), 8.37 (dd, J = 5 & 1 Hz, 1 H)

(3) Title compound (pale yellow crystals)

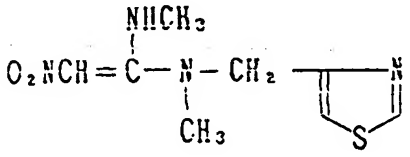
m.p.: 131-132 °C

NMR ($CDCl_3$) δ: 2.60 (s, MeS), 2.84 (s, $MeNCH_2$), 3.03 (d, J = 5 Hz, MeNH), 4.34 (s, CH_2), 6.57 (s, $=CHNO_2$), 7.07 (dd, J = 8 & 5 Hz, 1 H), 7.43 (dd, J = 8 & 1 Hz, 1 H), 8.46 (dd, J = 5 & 1 Hz, 1 H)

IR (Nujol): 1600, 1530, 1395, 1375, 1245 cm^{-1}

Example 70

1-Methylamino-1-[N-methyl-N-(4-thiazolyl)methyl]amino-2-nitroethylene (Compound 88)



The steps (1), (2) and (3) of Example 13 were repeated except that N-methyl-N-(4-thiazolyl)methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(4-thiazolylmethyl)thiourea (oil, crystallized on standing in a refrigerator)
(provided that the product was purified by silica gel column chromatography)

NMR ($CDCl_3$) δ: 3.15 (d, J = 5 Hz, MeNH), 3.30 (s, $MeNCH_2$), 4.98 (s, CH_2), 6.87 (br, NH), 7.38 (d, J = 2 Hz, 1 H), 8.81 (d, J = 2 Hz, 1 H)

(2) S-Methyl-N-methyl-N'-methyl-N'-(4-thiazolylmethyl)isothiourea (oil)

NMR ($CDCl_3$) δ: 2.31 (s, MeS), 2.91 (s, $MeNCH_2$), 3.27 (s, MeN =), 4.79 (s, CH_2), 7.17 (m, 1 H), 8.80 (d, J = 2 Hz, 1 H)

(3) Title compound (yellow crystals)
(provided that the reaction was conducted for 4.5 hours)

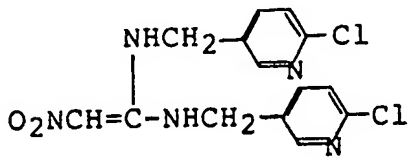
m.p.: 155-156 °C

NMR (DMSO-d_6) δ: 2.89 (s, $MeNCH_2$), 2.98 (d, J = 5 Hz, MeNH), 4.60 (s, CH_2), 6.55 (s, $=CHNO_2$), 7.70 (d, J = 2 Hz, 1 H), 8.95 (br q, J = 5 Hz, 1 H), 9.12 (d, J = 2 Hz, 1 H)

IR (Nujol): 1580, 1530, 1290, 1270, 1255 cm^{-1}

Example 71

1,1-bis(6-Chloro-3-pyridylmethyl)amino-2-nitroethylene (Compound 89)



(1) A mixture of 7.0 g (0.042 mole) of 1,1-bis(methylthio)-2-nitroethylene, 4.5 g of N,O-dimethylhydroxyamine hydrochloride and 80 ml of EtOH was refluxed and 6.4 ml of Et_3N was added dropwise over 1 hour. After completion of dropwise addition, the mixture was further refluxed for 2 hours. The reaction mixture was then concentrated and the resulting crystals were filtered off. The filtrate was concentratd and the residue was subjected to zilica gel column chromatography using EtOH-$CHCl_3$ (1:30) as the eluent. The procedure gave 1.0 g of 1-(N-methyl-N-methoxy)amino-1-methylthio-2-nitroethylene as a yellow oil.

NMR ($CDCl_3$) δ: 2.43 (3 H, s), 3.26 (3 H, s), 3.68 (3, H, s), 7.16 (1H, s)

(2) A mixture of 0.8 g (0.0045 mole) of 1-(N-methyl-N-methoxy)amino-1-methylthio-2-nitroethylene, 0.7 g of (6-chloro-3-pyridylmethyl)amine and 30 ml of EtOH was refluxed for 4 hours. The resulting crystals

were collected by filtration and dried to give 150 mg of the title compound as crystals.

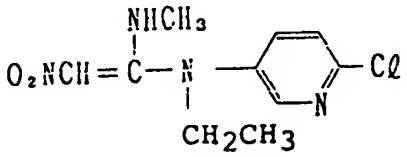
m.p.: 238-240 °C (decompn.)

NMR (DMSO-d_6) δ: 4.53 (4 H, d, J = 5.7 Hz), 6.51 (1 H, s), 7.50 (2 H, d, J = 8.7 Hz), 7.76 (2 H, dd, J = 8.7 & 2.4 Hz), 8.37 (2 H, d, J = 2.4 Hz), 9.7-10.8 (2 H, br)

IR (Nujol): 3240, 1620, 1575, 1460, 1395, 1220 cm^{-1}

Example 72

1-[N-(6-Chloro-3-pyridyl)-N-ethyl]amino-1-methylamino-2-nitroethylene (Compound 90)



(1) In 30 ml of toluene was dissolved 2.4 g (0.015 mole) of 2-chloro-5-ethylaminopyridine, followed by addition of 3.4 g of methyl isocyanate. The mixture was refluxed for 15 hours. After cooling, the resulting crystals were collected by filtration, washed with a small amount of Et_2O and dried. The procedure gave 3.0 g of N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylurea as pale yellow crystals.

m.p.: 135-136 °C

NMR ($CDCl_3$) δ: 1.11 (t, J = 7 Hz, 3 H), 2.75 (d, J = 5 Hz, 3 H), 3.72 (q, J = 7 Hz, 2 H), 4.36 (br, 1 H), 7.40 (d, J = 8 Hz, 1 H), 7.59 (dd, J = 8 & 3 Hz, 1 H), 8.28 (d, J = 3 Hz, 1 H)

(2) In 30 ml of CH_3CN was dissolved 1.5 g (0.007 mole) of N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylurea, followed by addition of 3.1 g of phosphorus pentasulfide. The mixture was refluxed for 3 hours. The insoluble matter was then filtered off and the filtrate was concentrated and diluted with 20 ml of water. The mixture was neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 (50 ml x 3) and the extract was dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography to recover 0.52 g of N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylthiourea as pale yellow crystals.

m.p.: 110-111 °C

NMR ($CDCl_3$) δ: 1.20 (t, J = 7 Hz, 3 H), 3.06 (d, J = 5 Hz, 3 H), 4.22 (q, J = 7 Hz, 2 H), 5.42 (br, 1 H), 7.40-7.70 (m, 2 H), 8.28 (d, J = 3 Hz, 1 H)

(3) The reaction procedure of Example 59 (2) was repeated except that N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylthiourea was used in lieu of N-(6-chloro-3-pyridyl)-N-methyl-N'-methylthiourea to give S-methyl-N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylisothiourea as a pale yellow oil.

NMR ($CDCl_3$) δ: 1.06-1.43 (m, 3 H), 2.02 & 2.39 (each s, 3 H), 3.03 & 3.30 (each s, 3 H), 3.46-3.93 (m, 2 H), 6.90-7.53 (m, 2 H), 7.88 & 8.20 (each d, J = 3 Hz, 1 H)

(4) The reaction procedure of Example 59 (3) was repeated except that S-methyl-N-(6-chloro-3-pyridyl)-N-ethyl-N'-methylisothiourea was used in lieu of S-methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-methylisothiourea to give the title compound as pale yellow crystals.

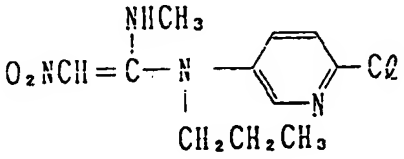
m.p.: 95-96 °C

NMR ($CDCl_3$) δ: 1.23 (t, J = 7 Hz, 3 H), 2.71 (d, J = 5 Hz, 3 H), 3.75 (q, J = 7 Hz, 2 H), 6.67 (s, 1 H), 7.26-7.53 (m, 2 H), 8.20 (d, J = 3 Hz, 1 H),10.05 (br, 1 H)

IR (Nujol): 3100, 1600, 1505, 1320, 1220, 1170, 1120, 1020 cm^{-1}

Example 73

1-[N-(6-Chloro-3-pyridyl)-N-n-propyl]amino-1-methylamino-2-nitroethylene (Compound 91)

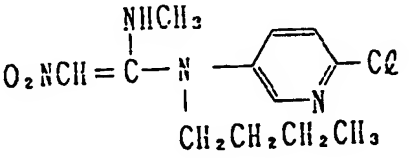


The steps (1), (2), (3) and (4) of Example 72 were repeated except that 2-chloro-5-n-propylaminopyridine was used in lieu of 2-chloro-5-ethylaminopyridine to obtain the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridyl)-N-n-propyl-N'-methylurea (pale yellow crystals)
m.p.: 84-85 °C
NMR ($CDCl_3$) δ: 0.87 (t, J = 7 Hz, 3 H), 1.26-1.80 (m, 2 H), 2.75 (d, J = 5 Hz, 3 H), 3.62 (t, J = 7 Hz, 2 H), 4.40 (br, 1 H), 7.38 (d, J = 8 Hz, 1 H), 7.66 (dd, J = 8 & 3 Hz, 1 H), 8.28 (d, J = 3 Hz, 1 H)
(2) N-(6-Chloro-3-pyridyl)-N-n-propyl-N'-methylthiourea(pale yellow crystals)
m.p.: 145-146 °C
NMR ($CDCl_3$) δ: 0.90 (t, J = 7 Hz, 3 H), 1.40-1.93 (m, 2 H), 3.07 (d, J = 5 Hz, 3 H), 4.12 (t, J = 7 Hz, 2 H), 5.33 (br, 1 H), 7.40-7.70 (m, 2 H), 8.30 (d, J = 3 Hz, 1H)
(3) S-Methyl-N-(6-chloro-3-pyridyl)-N-n-propyl-N'-methylisothiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 0.80-1.10 (m, 3 H), 1.40-1.90 (m, 2 H), 2.01 & 2.37 (each s, 3 H), 3.00 & 3.28 (each s, 3 H), 3.36-3.83 (m, 2 H), 6.90-7.53 (m, 2 H), 7.86 & 8.18 (each d, J = 3 Hz, 1H)
(4) Title compound (pale yellow crystals)
m.p.: 94-95 °C
NMR ($CDCl_3$) δ: 0.95 (t, J = 7 Hz, 3 H), 1.43-1.93 (m, 2 H), 2.68 (d, J = 5 Hz, 3 H), 3.61 (t, J = 7 Hz, 2 H), 6.69 (s, 1 H), 7.26-7.50 (m, 2 H), 8.21 (d, J = 3 Hz, 1 H), 10.06 (br, 1 H)
IR (Nujol): 3100, 1590, 1520, 1360, 1310, 1225, 1120, 1020 cm^{-1}

Example 74

1-[N-n-Butyl-N-(6-chloro-3-pyridyl)]amino-1-methyl-amino-2-nitroethylene (Compound 92)



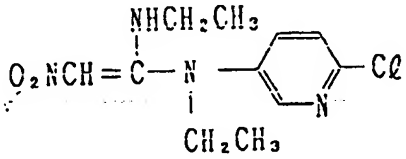
The steps (1), (2), (3) and (4) of Example 72 were repeated except that 2-chloro-5-n-butylaminopyridine was used in lieu of 2-chloro-5-ethylaminopyridine to give the following compounds in the respective steps.

(1) N-n-Butyl-N-(6-chloro-3-pyridyl)-N'-methylurea (pale yellow oil)
NMR ($CDCl_3$) δ: 0.86-1.06 (m, 3 H), 1.10-1.73 (m, 4 H), 2.75 (d, J = 5 Hz, 3 H), 3.66 (t, J = 7 Hz, 2 H), 4.30 (d, J = 5 Hz, 1 H), 7.40 (d, J = 8 Hz, 1 H), 7.60 (dd, J = 8 & 3 Hz, 1 H), 8.29 (d, J = 3 Hz, 1 H)
(2) N-n-Butyl-N-(6-chloro-3-pyridyl)-N'-methylthiourea (pale yellow crystals)
(provided that the reaction was conducted in toluene for 1 hour)
m.p.: 129-130 °C
NMR ($CDCl_3$) δ: 0.90 (t, J = 7 Hz, 3 H), 1.10-1.83 (m, 4 H), 3.07 (d, J = 5 Hz, 3 H), 4.15 (t, J = 7 Hz, 2 H), 5.52 (d, J = 5 Hz, 1 H), 7.36-7.70 (m, 2 H), 8.25 (d, J = 3 Hz, 1 H)
(3) S-Methyl-N-n-butyl-N-(6-chloro-3-pyridyl)-N'-methylisothiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 0.80-1.06 (m, 3 H), 1.10-1.80 (m, 4 H), 2.00 & 2.36 (each s, 3 H), 3.00 & 3.27 (each s, 3 H), 3.42-3.82 (m, 2 H), 6.90-7.50 (m, 2 H), 7.86 & 8.18 (each d, J = 3 Hz, 1 H)

(4) Title compound (pale yellow crystals)
m.p.: 87-88 °C
NMR ($CDCl_3$) δ: 0.93 (t, J = 7 Hz, 3 H), 1.10-1.85 (m, 4 H), 2.68 (d, J = 5 Hz, 3 H), 3.65 (t, J = 7 Hz, 2 H), 6.69 (s, 1 H), 7.26-7.52 (m, 2 H), 8.21 (d, J = 3 Hz, 1 H), 10.05 (br, 1 H)
IR (Nujol): 3100, 1590, 1520, 1360, 1310, 1250, 1120, 1020 cm^{-1}

Example 75

1-[N-(6-Chloro-3-pyridyl)-N-ethyl]amino-1-ethylamino-2-nitroethylene (Compound 93)

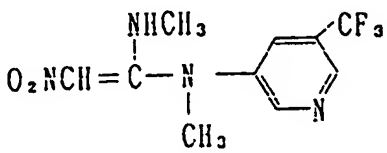


The steps (1), (2) and (3) of Example 59 were repeated except that 2-chloro-5-ethylaminopyridine and ethyl isothiocyanate were used in lieu of 2-chloro-5-methylaminopyridine and methyl isothiocyanate, respectively, to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridyl)-N-ethyl-N'-ethylthiourea (pale red crystals)
(provided that the reaction was conducted in toluene for 66 hours)
m.p.: 84-86 °C
NMR ($CDCl_3$) δ: 1.11 (3 H, t, J = 7.1 Hz), 1.19 (3 H, t, J = 7.2 Hz), 3.63 (2 H, dq, J = 5.6 & 7.1 Hz), 4.21 (2 H, q, J = 7.1 Hz), 4.9-5.5 (1 H, m, NH), 7.4-7.7 (2 H, m), 8.29 (1 H, d, J = 2.4 Hz)
(2) S-Methyl-N-(6-chloro-3-pyridyl)-N-ethyl-N'-ethylisothiourea (oil)
NMR ($CDCl_3$) δ: 1.0-1.6 (6 H, m), 2.00 & 2.38 (3 H, each s,), 3.1-4.5 (4 H, m), 6.8-7.6 (2 H, m), 7.7-8.5 (1 H, m)
(3) Title compound (pale yellow crystals)
m.p: 105 °C
NMR ($CDCl_3$) δ: 1.0-1.5 (6 H, m), 2.94 (2 H, dq, J = 5.2 & 7.0 Hz), 3.74 (2 H, q, J = 7.1 Hz), 6.65 (1 H, s), 7.2-7.6 (2 H, m), 8.1-8.4 (1 H, m), 9.6-10.2 (1 H, m, NH)
IR (Nujol): 3110, 1600 cm^{-1}

Example 76

1-Methylamino-1-[N-methyl-N-(5-trifluoromethyl-3-pyridyl)]amino-2-nitroethylene (Compound 94)



(1) The reaction procedure of Example 59 (1) was repeated except that 3-methylamino-5-trifluoromethylpyridine was used in lieu of 2-chloro-5-methylaminopyridine (refluxed in toluene for 61.5 hours) to give N-methyl-N'-methyl-N'-(5-trifluoromethyl-3-pyridyl)thiourea as pale brown crystals.
m.p.: 86-90 °C
NMR ($CDCl_3$) δ: 3.12 (3 H, d, J = 4.2 Hz), 3.67 (3 H, s), 5.3-5.8 (1 H, m, NH), 7.8-8.0 (1 H, m), 8.77 (1 H, d, J = 2.1 Hz), 8.88 (1 H, br s)
(2) A mixture of 0.2 g (0.0008 mole) of N-methyl-N'-methyl-N'-(5-trifluoromethyl-3-pyridyl)thiourea, 0.3 g of methyl iodide and 10 ml of CH_3CN was stirred at room temperature for 13.5 hours. Then, 0.3 g of methyl iodide was further added and the mixture was stirred for 18.5 hours. The reaction mixture was concentrated and the residue was diluted with 50 ml of AcOEt and aqueous sodium hydrogen carbonate solution. After shaking, the mixture was subjected to phase separation. The AcOEt layer was washed with

aqueous sodium chloride solution, dried over $MgSO_4$ and concentrated. The procedure gave 0.2 g of crude S-methyl-N-methyl-N'-nethyl-N'-(5-trifluoromethyl-3-pyridyl)isothiourea as oil.

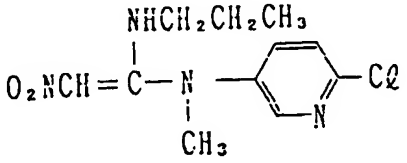
(3) A mixture of 0.2 g of crude S-methyl-N-metyl-N'-methyl-N'-(5-trifluoromethyl-3-pyridyl)isothiourea and 10 ml of CH_3NO_2 was refluxed for 36.5 hours. The reaction mixture was concentrated and the residue was subjected to silica gel column chromatography using hexane-acetone (2:1) as the eluent. The procedure gave 18 mg of the title compound as yellow-brown crystals.

m.p: 114-115 °C

NMR ($CDCl_3$) δ: 2.81 (3 H, d, J = 5.1 Hz), 3.36 (3 H, s), 6.63 (1 H, s), 7.5-7.7 (1 H, m), 8.5-8.7 (2 H, m), 9.6-10.1 (1 H, m, NH)

Example 77

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-n-propyl-amino-2-nitroethylene (Compound 95)



The steps (1), (2) and (3) of Example 59 were repeated except that n-propyl isothiocyanate was used in lieu of methyl isothiocyanate to give the following compounds in the respective steps.

(1) N-(6-Chloro-3-pyridyl)-N-methyl-N'-n-propylthiourea(yellow oil)

(provided that the reaction mixture was refluxed in toluene for 121 hours and the product was purified by silica gel column chromatography)

NMR ($CDCl_3$) δ: 0.86 (3 H, t, J = 6.6 Hz), 1.2-1.8 (2 H, m), 3.63 (3 H, s), 3.4-3.9 (2 H, m), 5.1-5.7 (1 H, br), 7.45 (1 H, d, J = 8.4 Hz), 7.61 (1 H, dd, J = 8.4 & 2.7 Hz), 8.34 (1 H, d, J = 2.7 Hz)

(2) S-Methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-n-propylisothiourea (yellow oil)

NMR ($CDCl_3$) δ: [major component•••74%] 0.96 (3 H, t, J = 7.5 Hz), 1.3-1.9 (2 H, m), 2.03 (3 H, s), 3.28 (3 H, s), 3.47 (2 H, t, J = 7.5 Hz), 7.25 (1 H, d, J = 8.4 Hz), 7.45 (1 H, dd, J = 8.4 & 2.7 Hz), 8.23 (1 H, d, J = 2.7 Hz) [minor component (isomer)•••26%] 2.38 (3 H, s), 3.14 (3 H, s), 3.0-3.4 (2 H, m), 6.9-7.4 (2 H, m)

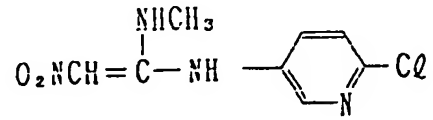
(4) Title compound (oil)

NMR ($CDCl_3$) δ: 0.93 (3 H, t, J = 7.2 Hz), 1.59 (2 H, tq, J = 7.2 & 7.2 Hz), 2.95 (2 H, dt, J = 6.0 & 7.2 Hz), 3.30 (3 H, s), 6.60 (1 H, s), 7.2-7.6 (2 H, m), 8.23 (1 H, d, J = 3.0 Hz), 9.6-10.1 (1 H, br)

IR (neat): 3110, 2950, 1595, 1450, 1360 cm^{-1}

Example 78

1-(6-Chloro-3-pyridyl)amino-1-methylamino-2-nitroethylene (Compound 96)



(1) A mixture of 3.9 g (0.0303 mole) of 5-amino-2-chloropyridine, 5.0 g of 1,1-bis(methylthio)-2-nitroethylene and 80 ml of ethylbenzene was heated at 130 °C for 2 hours. The ethylbenzene was distilled off under reduced pressure and the crystalline residue was washed with AcOEt and subjected to silica gel column chromatography using EtOH-$CHCl_3$ (1:30) as the eluent to recover crude crystals. These crystals were recrystallized from AcOEt, washed with ether and dried. The procedure save 0.5 g of 1-(6-chloro-3-pyridyl)amino-1-methylthio-2-nitroethylene as pale yellow crystals.

m.p.: 169-171 °C

NMR ($CDCl_3$) δ: 2.42 (3 H, s), 6.70 (1 H, s), 7.41 (1 H, d, J = 9.0 Hz), 7.65 (1 H, dd, J = 9.0 & 2.4 Hz),

8.41 (1 H, d, J = 2.4 Hz), 11.3-11.8 (1 H, br)

(2) In 25 ml of EtOH was dissolved 0.42 g (0.00171 mole) of 1-(6-chloro-3-pyridyl)amino-1-methylthio-2-nitroethylene, followed by addition of 0.2 g of a 40% solution of methylamine in methanol. The mixture was refluxed for 1.5 hours. The solvent was distilled off and the crystalline residue was washed with AcOEt and dried to recover 0.33 g of the title compound as white crystals.

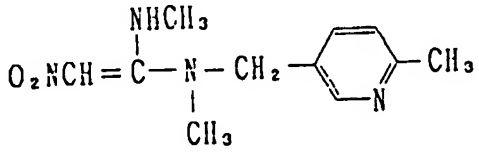
m.p.: 185 °C (decompn.)

NMR (DMSO-d_6) δ: 2.94 (3 H, d, J = 5.4 Hz), 6.24 (1 H, s), 7.57 (1 H, d, J = 9.0 Hz), 7.80 (1 H, dd, J = 9.0 & 2.7 Hz), 8.34 (1 H, d, J = 2.7 Hz), 8.8-9.7 (1 H, br), 9.2-10.3 (1 H, br)

IR (Nujol): 3150, 1635, 1210 cm^{-1}

Example 79

1-Methylamino-1-[N-methyl-N-(6-methyl-3-pyridyl-methyl)]amino-2-nitroethylene (Compound 97)



The steps (1), (2) and (3) of Example 13 were repeated except that crude N-methyl-N-(6-methyl-3-pyridylmethyl)amine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-Methyl-N'-methyl-N'-(6-methyl-3-pyridylmethyl)-thiourea (pale pink crystals)

m.p.: 120-122 °C

NMR ($CDCl_3$) δ: 2.53 (s, pyridine-Me), 3.06 (s, $MeNCH_2$), 3.16 (d, J = 5 Hz, MeNH), 5.16 (s, CH_2), 6.14 (br q, J = 5 Hz, NH), 7.15 (d, J = 8 Hz, 1 H), 7.64 (dd, J = 8 & 2 Hz, 1H), 8.40 (d, J = 2 Hz, 1H)

(2) S-Methyl-N-methyl-N'-methyl-N'-(6-methyl-3-pyridyl-methyl)isothiourea (oil)

NMR ($CDCl_3$) δ: 2.31 (s, MeS), 2.53 (s, pyridine-Me), 2.81 (s, $MeNCH_2$), 3.25 (s, NeN=), 4.53 (s, CH_2), 7.11 (d, J = 8 Hz, 1 H), 7.48 (dd, J = 8 & 2 Hz, 1 H), 8.40 (d, J = 2 Hz, 1 H)

(3) Title compound (yellow crystals)

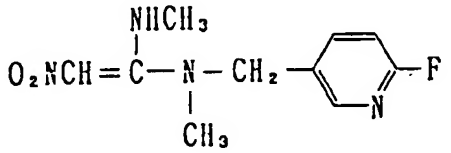
m.p.: 102-103 °C

NMR ($CDCl_3$) δ: 2.57 (s, pyridine-Me), 2.80 (s, $MeNCH_2$), 3.08 (d, J = 5 Hz, MeNH), 4.39 (s, CH_2), 6.54 (s, $=CHNO_2$), 7.21 (d, J = 8 Hz, 1 H), 7.48 (dd, J = 8 & 2 Hz, 1 H), 9.78 (br, NH)

IR (Nujol): 1600, 1550, 1310, 1250, 1090 cm^{-1}

Example 80

1-[N-(6-Fluoro-3-pyridylmethyl)-N-methyl]amino-1-nethylamino-2-nitroethylene (Compound 95)



The steps (1), (2) and (3) of Example 13 were vepeated except that crude N-(6-fluoro-3-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridyl-methyl)amine to give the following compounds in the respective steps.

(1) N-(6-Fluoro-3-pyridylmethyl)-N-methyl-N'-methylthiourea (colorless oil)

(provided that the reaction was conducted in $CHCl_3$ overnight and the product was purified by silica gel column chromatography)

NMR ($CDCl_3$) δ: 3.04 (3 H, s, $MeNCH_2$), 3.18 (3 H, d, MeNH), 5.22 (2 H, s, CH_2), 6.88 (1 H, br, NH), 7.93 (1 H, dd, J = 8.4 & 2.7 Hz), 8.54 (1 M, ddd, J = 8.4, 2.4 & 8.4 Hz), 8.15 (1 H, d, J = 2.4 Hz)

(2) S-Methyl-N-(6-fluoro-3-pyridylmethyl)-N-methyl-N'-methylisothiourea (oil)

NMR ($CDCl_3$) δ: 2.30 (3 H, s, MeS), 2.83 (3 H, s, $MeNCH_2$), 3.24 (3 H, s, MeN=), 4.53 (2 H, s, CH_2), 6.90 (1 H, dd), 7.72 (1 H, ddd), 8.12 (1 H, d)

(3) Title compound (pale brown crystals)

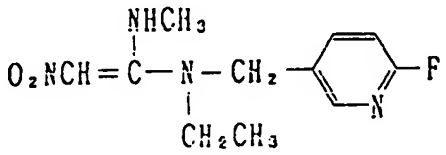
m.p.: 100-100.5 °C

NMR ($CDCl_3$) δ: 2.78 (3 H, s, $MeNCH_2$), 3.07 (3 H, d,MeNH), 4.39 (2 H, s, CH_2), 6.52 (1 H, s, $=CHNO_2$), 7.00 (1 H, dd, J=8.4 & 2.7 Hz), 7.71 (1 H, ddd, J=8.4, 2.4 & 8.4 Hz), 8.14 (1 H, d, J=2.4 Hz), 9.74 (1 H, br, NH)

IR (Nujol): 1593, 1548, 1477, 1465, 1437, 1405, 1390, 1310, 1250, 1230, 1165, 1083, 1029 cm^{-1}

Example 81

1-[N-Ethyl-N-(6-fluoro-3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene (Compound 99)



(1) In 30 ml of CH_3CN was dissolved 4.2 g of 70% aqueous ethylamine solution and 3.0 g (0.016 mole in terms of pure product) of crude (6-fluoro-3-pyridyl)methyl bromide was added bropwise thereto under ice-cooling. The mixture was allowed to stand at room temperature overnight and the CH_3CN was distilled off. The residue was diluted with 20 ml of water and extracted with $CHCl_3$ (30 ml). The extract was dried over $MgSO_4$ and the $CHCl_3$ was distilled off to recover 1.38 g of red oil. This oil was dissolved in 30 ml of $CHCl_3$, followed by addition of 0.68 g of methyl isothiocyanate. The mixture was stirred at room temperature for 3 hours. The reaction mixture was treated with activated carbon and concentrated and the residue was subjected to silica gel column chromatography using AcOEt-hexane (3.5:1) as the eluent. The procedure gave 0.6 g of N-ethyl-N-(6-fluoro-3-pyridylmethyl)-N'-methylthiourea as colorless crystals.

m.p.: 123-124 °C

NMR ($CDCl_3$) δ: 1.18 (3 H, t, CH_2CH_3), 3.19 (3 H, d, MeNH), 3.48 (2 H, q, CH_2CH_3), 5.15 (2 H, s, pyridine-CH_2), 5.70 (1 H, br, NH), 6.92 (1 H, dd, J=8.4 & 2.7 Hz), 7.96 (1 H, ddd, J=8.4, 2.4 & 8.4 Hz), 8.15 (1 H, d, J=2.4 Hz)

(2) The reaction procedure of Example 13 (2) was repeated except that N-ethyl-N-(6-fluoro-3-pyridylmethyl)-N'-methylthiourea was used in lieu of N-methyl-N'-ethyl-N'-(3-pyridylmethyl)thiourea to give S-methyl-N-ethyl-N-(6-fluoro-3-pyridylmethyl)-N'-methylisothiourea as a pale brown oil.

NMR ($CDCl_3$) δ: 1.08 (3 H, t, CH_2CH_3), 2.29 (3 H, s, MeS), 3.22 (3 H, s, MeN=), 3.36 (2 H, q, CH_2CH_3), 4.49 (2 H, s, CH_2), 6.87 (1 H, dd), 7.71 (1 H, ddd), 8.11 (1 H, d)

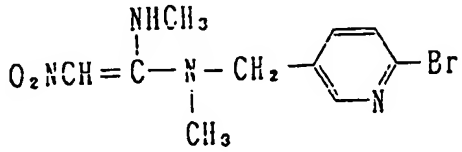
(3) The reaction procedure of Example 13 (3) was repeated except that S-methyl-N-ethyl-N-(6-fluoro-3-pyridylmethyl)-N'-methylisothiourea was used in lieu of S-methyl-N-methyl-N'-ethyl-N'-(3-pyridylmethyl)-isothiorea to give the title compound as oil.

NMR ($CDCl_3$) δ: 1.19 (3 H, t, CH_2CH_3), 3.08 (3 H, d, MeNH), 3.16 (2 H, q, CH_2CH_3), 4.37 (2 H, s, CH_2), 6.54 (1 H, s, $=CHNO_2$), 6.98 (1 H, dd, J=8.4 & 2.7 Hz), 7.80 (1 H, ddd, J=8.4, 2.4 & 8.4 Hz), 8.15 (1 H, d, J=2.4 Hz)

IR (neat): 3230, 1593, 1510, 1480, 1395, 1335, 1235, 1120, 1020 cm^{-1}

Example 82

1-[N-(6-Bromo-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 100)

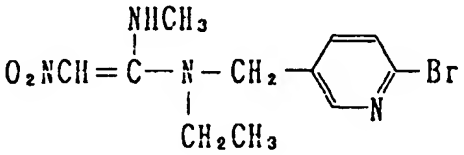


The steps (1), (2) and (3) of Example 13 were repeated except that crude N-(6-bromo-3-pyridylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(6-Bromo-3-pyridylmethyl)-N-methyl-N'-methylthiourea (white crystals)
(provided that the product was purified by silica gel column chromatography)
m.p.: 107-108 °C
NMR ($CDCl_3$) δ: 3.04 (3 H, s), 3.18 (3 H, d, J = 4.8 Hz), 5.19 (2 H, s), 5.6-6.1 (1 H, br), 7.46 (1 H, d, J = 8.4 Hz), 7.66 (1 H, dd, J = 8.4 & 2.4 Hz), 8.29 (1 H, d, J = 2.4 Hz)
(2) S-Methyl-N-(6-bromo-3-pyridylmethyl)-N-methyl-N'-methylisothiourea (colorless oil)
NMR ($CDCl_3$) δ: 2.29 (3 H, s), 2.84 (3 H, s), 3.23 (3 H, s), 4.50 (2 H, s), 7.3-7.6 (2 H, m), 8.29 (1 H, d, J = 2.4 Hz)
(3) Title compound (pale brown crystals)
m.p.: 130-131 °C
NMR ($CDCl_3$) δ: 2.80 (3 H, s), 3.06 (3 H, d, J = 5.4 Hz), 4.36 (2 H, s), 6.51 (1 H, s), 7.35-7.70 (2 H, m), 8.2-8.4 (1 H, m), 9.4-10.0 (1 H, br)
IR (Nujol): 3200, 1580, 1390, 1280, 1245, 1205, 1075 cm^{-1}

Example 83

1-[N-(6-Bromo-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene (Compound 101)

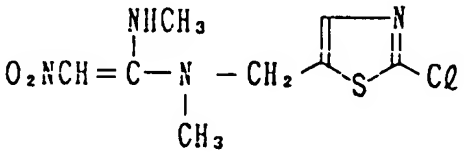


The steps (1), (2) and (3) of Example 13 were repeated except that crude N-(6-bromo-3-pyridylmethyl)-N-ethylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

(1) N-(6-Bromo-3-pyridylmethly)-N-ethyl-N'-methylthiourea(pale yellow crystals)
m.p.: 130-131 °C
NMR ($CDCl_3$) δ: 1.18 (3 H, t, J = 7.8 Hz), 3.18 (3 H, d, J = 5.0 Hz), 3.46 (2 H, q, J = 7.8 Hz), 5.12 (2 H, s), 5.5-6.0 (1 H, br), 7.46 (1 H, d, J = 8.7 Hz), 7.69 (1 H, dd, J = 8.7 & 2.1 Hz), 8.29 (1 H, d, J = 2.1 Hz)
(2) S-Methyl-N-(6-bromo-3-pyridylmethyl)-N-ethyl-N'-methylisothiourea (yellow oil)
NMR ($CDCl_3$) δ: 1.08 (3 H, t, J = 6.3 Hz), 2.29 (3 H, s), 3.21 (3 H, s), 3.36 (2 H, q, J = 6.3 Hz), 4.46 (2 H, s), 7.3-7.6 (2 H, m), 8.28 (1 H, br s)
(3) Title compound
(provided that the reaction was conducted for 38 hours)
m.p.: 79-80 °C
NMR ($CDCl_3$) δ: 1.18 (3 H, t, J = 6.3 Hz), 3.06 (3 H, d, J = 5.7 Hz), 3.16 (2 H, q, J = 6.3 Hz), 4.34 (2 H, s), 6.53 (1 H, s), 7.3-7.7 (2 H, m), 8.30 (1 H, br s), 9.5-10.1 (1 H, br q, J = 5.7 Hz)
IR (Nujol): 3200, 1580, 1240, 1080 cm^{-1}

Example 84

1-[N-(2-Chloro-5-thiazolylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 102)



The steps (1), (2) and (3) of Example 13 were repeated except that crude N-(2-chloro-5-thiazolylmethyl)-N-methylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

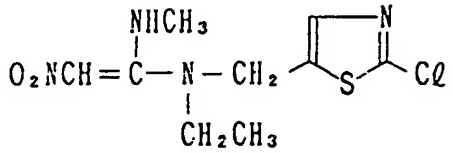
(1) N-(2-Chloro-5-thiazolylmethyl)-N-methyl-N'-methylthiourea (white - pale brown crystals)
(provided that a silica gel column was used for purification)
m.p.: 129-131 °C
NMR ($CDCl_3$) δ: 3.06 (s, $\underline{Me}NCH_2$), 3,16 (d, J = 4 Hz, $\underline{Me}NH$), 5.21 (s, CH_2), 5.83 (br, NH), 7.48 (s, thiazole-H)

(2) S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N-methyl-N'-methylisothiourea (yellow oil)
NMR ($CDCl_3$) δ: 2.30 (s, MeS), 2.90 (s, $\underline{Me}NCH_2$), 3.24 (s, MeN =), 4.50 (s, CH_2), 7.39 (s, thiazole-H)

(3) Title compound (pale brown crystals)
m.p.: 131-133 °C
NMR ($CDCl_3$) δ: 2.84 (s, $\underline{Me}NCH_2$), 3.09 (d, J = 5 Hz, $\underline{Me}N$ =), 4.49 (s, CH_2), 6.51 (s, $=CHNO_2$), 7.50 (s, thiazole-H), 9.66 (br, NH)
IR (Nujol): 1585, 1395, 1260, 1070, 1050, 1025 cm^{-1}

Example 85

1-[N-(2-Chloro-5-thiazolylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene (Compound 103)



The steps (1), (2) and (3) of Example 13 were repeated except that crude N-(2-chloro-5-thiazolylmethyl)-N-ethylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine to give the following compounds in the respective steps.

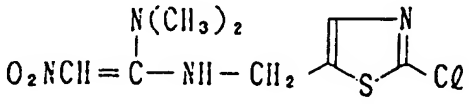
(1) N-(2-Chloro-5-thiazolylmethyl)-N-ethyl-N'-methylthiourea (white crystals)
m.p.: 116-118 °C
NMR ($CDCl_3$) δ: 1.19 (t, J = 7 Hz, $CH_2\underline{CH_3}$), 3.16 (d, J = 4 Hz, $\underline{Me}NH$), 3,44 (q, J = 7 Hz, $\underline{CH_2}CH_3$), 5.15 (s, thiazole-CH_2), 5.79 (br, NH), 7.47 (thiazole-H)

(2) S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N-ethyl-N'-methylisothiourea (oil)
NMR ($CDCl_3$) δ: 1.11 (t, J = 7 Hz, $CH_2\underline{CH_3}$), 2.28 (s, MeS), 3.26 (s, MeN), 3.40 (q, J = 7 Hz, $\underline{CH_2}CH_3$), 4.50 (s, thiazole-CH_2), 7.39 (s, thiazole-H)

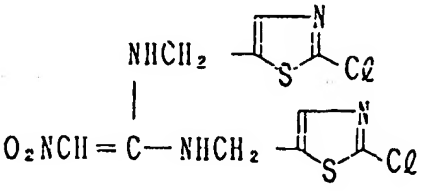
(3) Title compound (pale brown crystals)
(provided that the reaction was conducted for 24 hours).
m.p.: 91-92 °C (this product was recrystallized from AcOEt-hexane to give product indicating m.p. 110-112 °C)
NMR ($CDCl_3$) δ: 1.18 (t, J = 7 Hz, $CH_2\underline{CH_3}$), 3.07 (d, J = 5 Hz, $\underline{Me}NH$), 3.17 (q, J = 7 Hz, $\underline{CH_2}CH_3$), 4,46 (s, thiazole-CH_2), 6.52 (s, $=CHNO_2$), 7.47 (s, thiazole-H); 9.75 (br, NH)
IR (Nujol): 1585, 1450, 1405, 1360, 1255, 1225, 1050 cm^{-1}

Example 86

1-(2-Chloro-5-thiazolylmethyl)amino-1-dimethylamino-2-nitroethylene (Compound 104) and 1,1-bis(2-chloro-5-thiazolylmethyl)amino-2-nitroethylene (Compound 105)



(Compound 104)



(Compound 105)

A mixture of 0.60 g (0.0037 mole) of 1-dimethylamino-1-methylthio-2-nitroethylene, 0.55 g of 2-chlor-5-thiazolymethylamine and 30 ml of EtOH was refluxed for 1.5 hours. After cooling, the resulting crystals of 1-N-(2-chloro-5-thiazolylmethyl)amino-1-methylthio-2-nitroethylene (0.20 g) were filtered off and the filtrate was concentrated and subjected to silica gel column chromatography using EtOH-$CHCl_3$ (1:10) as the eluent. The procedure gave 0.07 g of the title compound (Compound 104) and 0.034 g of the title compound (Compound 105).

(1-(2-Chloro-5-thiazolylmethyl)amino-1-methylthio-2-nitroethylene)

m.p.: 150-152 °C

NMR ($CDCl_3$) δ: 2.49 (3 H, s), 4.78 (2 H, d, J = 6.0 Hz), 6.58 (1 H, s), 7.52 (1 H, s),10.3-10.8 (1 H, br)

(Compound 104)

m.p.: 101-102 °C

NMR ($CDCl_3$) δ: 2.97 (6 H, s), 4.58 (2 H, d, J = 6.3 Hz), 6.51 (1 H, s), 7.50 (1 H, s), 9.3-9.8 (1 H, br)

IR (Nujol): 3100, 1585, 1380, 1255, 1030 cm^{-1}

(Compound 105)

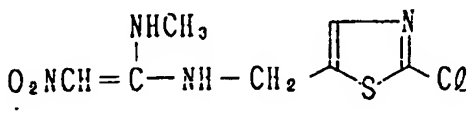
m.p.: 211 °C (decompn.)

NMR (DMSO-d_6) δ: 4.5-4.8 (4 H, m), 6.63 (1 H, s), 7.63 (2 H, s)

IR (Nujol): 3120, 1610, 1210, 1040 cm^{-1}

Example 87

1-(2-Chloro-5-thiazolylmethyl)amino-1-methylamino-2-nitroethylene (Compound 106)



A mixture of 0.19 g (0.00072 mole) of the 1-N-(2-chloro-5-thiazolylmethyl)amino-1-methylthio-2-nitroethylene prepared in Example 86 and 25 ml of EtOH was heated at 70 °C. Then 0.1 g of a 40% aqueous solution of methylamine was added and the mixture was stirred at 70 °C for 0.5 hour. The EtOH was distilled off, and after addition of AcOEt, the crystalline residue was filtered and dried. The procedure gave 0.12 g of the title compound as white crystals.

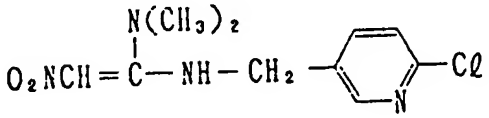
m.p.: 181 °C (decompn.)

NMR (DMSO-d_6) δ: 2.83 (3 H, d, J = 5.1 Hz), 4.63 (2 H, d, J = 6.3 Hz), 6.57 (1 H, s), 7.66 (1 H, s), 7.3-8.1 (1 H, br), 9.6-10.4 (1 H, br)

IR (Nujol): 3140, 1620, 1415, 1210 cm^{-1}

Example 88

1-(6-Chloro-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene (Compound 46)



(1) A mixture of 4.32 g (0.0303 mole) of 6-chloro-3-pyridylmethylamine, 20 ml of water and 1.78 g of sodium hydroxide was stirred at room temperature and 2.37 ml of carbon disulfide was added dropwise. After completion of dropwise addition, the mixture was further stirred at 50 °C for 1 hour. After cooling with ice-water, 3.49 ml of ethyl chlorocarbonate was added dropwise at about 5 °C. After completion of dropwise addition, the mixture was stirred at 50 °C for 1 hour. After cooling, the reaction mixture was saturated with sodium chloride and extracted with Et_2O (50 ml x 3), and the extract and dried over $MgSO_4$. Then, the Et_2O was distilled off to recover 5.38 g of crude (6-chloro-3-pyridyl)methyl isothiocyanate as oil.

NMR ($CDCl_3$) δ: 4.77 (s, CH_2), 7.39 (d, J = 8 Hz, 1 H), 7.70 (dd, J = 8 & 2 Hz, 1 H), 8.36 (d, J = 2 Hz, 1 H)

(2) A mixture of 5.16 g of a 50% aqueous solution of dimethylamine and 30 ml of CH_3CN was stirred under cooling with ice-water. Then, a solution of 5.29 g (0.0287 mole in terms of pure product) of crude (6-chloro-3-pyridyl)-methyl isothiocyanate in 30 ml of CH_3CN was added dropwise thereto. After completion of dropwise addition, the mixture was stirred at room temperature for 15 minutes. The CH_3CN was distilled off and the residue was diluted with aqueous sodium chloride solution and extracted with CH_2Cl_2 (50 ml x 3). The cxtract was dried over $MgSO_4$ and the CH_2Cl_2 was distilled off, whereupon crystals were obtained. After addition of Et_2O, the crystals were collected by filtration, dried and recrystallized from AcOEt. The procedure gave 3.82 g of N-(6-chloro-3-pyridylmethyl)N'-dimethylthiourea as yellow crystals.

m.p.: 139-141 °C

NMR ($CDCl_3$) δ: 3.27 (s, Me_2N), 4.88 (d, J = 5 Hz, CH_2), 6.17 (br t, J = 5 Hz, NH), 7.27 (d, J = 8 Hz, 1 H), 7.76 (dd, J = 8 & 2 Hz, 1 H), 8.25 (d, J = 2 Hz, 1 H)

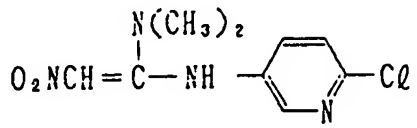
(3) To 3.00 g (0.013 mole) of N-(6-chloro-3-pyridyl-methyl)-N'-dimethylthiourea was added 32 ml of dry THF, followed by addition of 0.52 g of 60% sodium hydride. The mixture was stirred at 50 °C for 15 minutes. After cooling with ice-water, 0.814 ml of methyl iodide was added dropwise and the mixture was stirred at room temperature for 20 minutes. The THF was distilled off and the residue was diluted with aqueous sodium chloride solution and extracted with AcOEt (50 ml x 3). The extract was dried over $MgSO_4$ and the AcOEt was distilled off. The procedure gave 3.30 g of crude S-methyl-N-(6-chloro-3-pyridylmethyl)-N'-dimethylisothiourea as oil.

NMR ($CDCl_3$) δ: 2.30 (s, MeS), 2.98 (s, Me_2N), 4.69 (s, CH_2), 7.25 (d, J = 8 Hz, 1 H), 7.65 (dd, J = 8 & 2 Hz, 1 H), 8.37 (d, J = 2 Hz, 1 H)

(4) To 3.24 g (0.0133 mole in terms of pure products) of crude S-methyl-N-(6-chloro-3-pyridylmethyl)-N'-dimethylisothiourea was added 14.5 ml of CH_3NO_2 and the mixture was refluxed with stirring for 14.5 hours. The CH_3NO_2 was then distilled off and the residue vas subjected to silica gel (240 g) column chromatography using MeOH-$CHCl_3$ (1:5) as the eluent to recover an oil. This oil was dissolved in AcOEt, the AcOEt was distilled off, and the residue was allowed to stand, whereupon crystals separated out. After addition of Et_2O, the crystals were recovered by filtration, washed with Et_2O and dried. The procedure gave 2.30 g of the title compound as pale yellow crystals. This product was in agreement with Compound 46 obtained in Example 28 in melting point, NMR and IR spectra and TLC Rf.

Example 89

1-(6-Chloro-3-pyridyl)amino-1-dimethylamino-2-nitroethylene (Compound 107)



A mixture of 1.5 g (0.0093 mole) of 1-dimethylamino-1-methylthio-2-nitroethylene and 1.1 g of 5-amino-2-chloropyridine was heated at 110-120 °C with stirring for 1 hour. After cooling, the reaction mixture was subjected to silica gel column chromatography using EtOH-$CHCl_3$ (1:40) as the eluent to recover 0.38 g of the title compound as pale brown crystals. The NMR spectrum of this product showed that it was a 1:1 mixture of the title compound and N^2-(6-chloro-3-pyridyl)-N'-dimethyl-2-nitroacetamidine.

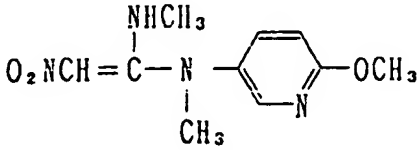
m.p.: 122-123 °C

NMR ($CDCl_3$) δ: 2.86 (3 H, s), 3.10 (3 H, s), 5.17 (1 H, s), 6.68 (0.5 H, s), 7.09 (0.5 H, dd, J = 9.0 & 2.7 Hz), 7.24 (0.5 H, d, J = 9.0 Hz), 7.3-7.6 (1 H, m), 7.86 (0.5 H, d, J = 2.7 Hz), 8.22 (0.5 H, d, J = 2.7 Hz), 10.8-11.2 (0.5 H, br)

IR (Nujol): 3100, 1395, 1280 cm^{-1}

Example 90

1-[N-(6-Methoxy-3-pyridyl)-N-methyl]amino-1-methylamino-2-nitroethylene (Compound 108)



The steps (1), (2) and (3) of Example 59 were repeated except that 2-methoxy-5-methylaminopyridine was used in lieu of 2-chloro-5-methylaminopyridine to give the following compounds in the respective steps.

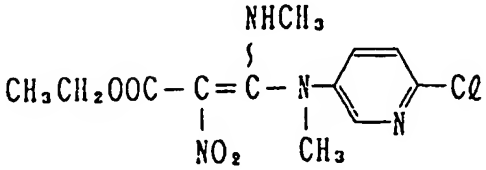
(1) N-(6-Methoxy-3-pyridyl)-N-methyl-N'-methylthiourea (white crystals)
(provided that the reaction was conducted in toluene)
m.p.: 115.5-116 °C
NMR ($CDCl_3$) δ: 3.06 (3 H, d, J = 4.5 Hz), 3.65 (3 H, s), 3.97 (3 H, s), 5.2-5.8 (1 H, m, NH), 6.86 (1 H, d, J = 8.7 Hz), 7.46 (1 H, dd, J = 9.0 & 3.0 Hz), 8.08 (1 H, d, J = 2.4 Hz)

(2) S-Methyl-N-(6-methoxy-3-pyridyl)-N-methyl-N'-methylisothiourea (pale yellow oil)
NMR ($CDCl_3$) δ: 2.01 (3 H, s), 3.18 (3 H, s), 3.28 (3 H, s), 3.93 (3 H, s,), 6.72 (1 H, d, J = 9.0 Hz), 7.43 (1 H, dd, J = 9.0 & 3.0 Hz), 8.02 (1 H, d, J = 2.4 Hz)

(3) Title compound (yellow crystals)
(provided that the reaction was conducted for 16 hours)
m.p.: 131-132 °C
NMR ($CDCl_3$) δ: 2.65 (3 H, d, J = 5.4Hz), 3.27 (3 H, s), 3.96 (3 H, s), 6.07 (1H, s), 6.82 (1 H, d, J = 9.0 Hz), 7.43 (1 H, dd, J = 8.4 & 3.0 Hz), 8.04 (1 H, d, J = 2.7 Hz), 9.8-10.4 (1 H, m)
IR (Nujol): 3130, 1590 cm^{-1}

Example 91

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-methyl-amino-2-ethoxycarbonyl-2-nitroethylene (Compound 109)



A mixture of 2.0 g (0.0087 mole) of S-methyl-N-(6-chloro-3-pyridyl)-N-methyl-N'-methylisothiourea and 4.0 g of ethyl nitroacetate was stirred with heating at 90-100 °C for 6 hours. After cooling, a small amount of acetone was added and the resulting crystals were collected by filtration, washed with acetone and dried. The procedure gave 0.3 g of the title compound as white crystals. From the filtrate, acetone was distilled off and the residue was further stirred with heating at 90-100 °C for 16 hours. The procedure gave a furhter crop (0.2 g) of the title compound.

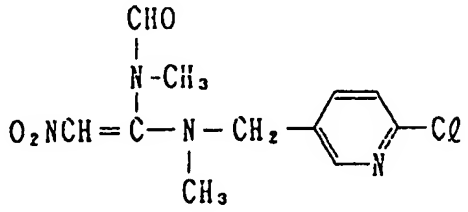
m.p.: 225-227 °C (decompn.)

NMR (DMSO-d_6) δ: 1.10 (3 H, t, J = 6.9 Hz), 2.89 (3 H, s), 3.45 (3 H, s), 3.93 (2 H, q, J = 7.3 Hz), 7.60 (1 H, d, J = 8.4 Hz), 7.75 (1 H, dd, J = 8.1 & 2.7 Hz), 8.30 (1 H, d, J = 2.1 Hz), 9.31 (1 H, br s)

IR (Nujol): 3190, 1675, 1630 cm^{-1}

Example 92

1-[N-(6-Chloro-3-pyridylmethyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 110)



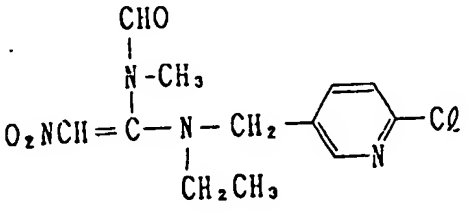
The reaction procedure of Example 46 was repeated except that 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]-amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene to give the title compound as a yellow resinous mass.

NMR (DMSO-d_6) δ: 2.92 (s, 3 H), 3.03 (s, 3 H), 4.60 (br, 2 H), 6.86 (s, 1 H), 7.48 (d, J = 8 Hz, 1 H), 7.80 (dd, J = 8 & 2 Hz, 1 H), 8.23 (s, 1 H), 8.38 (d, J = 2 Hz, 1 H)

IR (neat): 1690, 1560, 1490, 1350, 1270, 1100 cm^{-1}

Example 93

1-[N-(6-Chloro-3-pyridylmethyl)-N-ethyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 111)



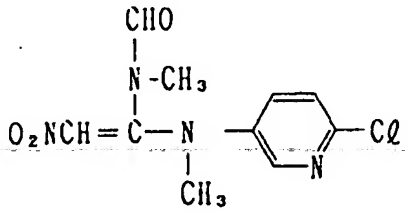
The reaction procedure of Example 46 was repeated except that 1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene to give the title compound as a yellow resinous mass.

NMR (DMSO-d_6) δ: 1.13 (t, J = 7 Hz, 3 H), 3.00 (s, 3 H), 3.10-3.53 (m, 2 H), 4.60 (br, 2 H), 6.96 (s, 1 H), 7.48 (d, J = 8 Hz, 1 H), 7.82 (dd, J = 8 & 2 Hz, 1 H), 8.20 (s, 1 H), 8.39 (d, J = 2 Hz, 1 H)

IR (neat): 1685, 1560, 1480, 1340, 1240, 1100 cm^{-1}

Example 94

1-[N-(6-Chloro-3-pyridyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 112)



The reaction procedure of Example 46 was repeated cxcept that 1-[N-(6-chloro-3-pyridyl)-N-methyl]-amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]-amino-2-nitroethylene to give the title compound as yellow crystals.

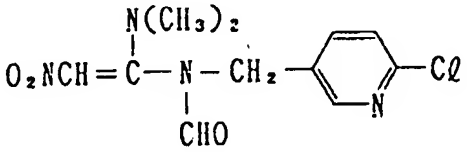
m.p.: 134-135 °C

NMR (DMSO-d_6) δ: 2.73 & 2.89 (each s, 3 H), 3.32 & 3.39 (each s, 3 H), 7.03 & 7.10 (each s, 1 H), 7.46 & 7.57 (each d, J = 8 Hz, 1 H), 7.83 & 7.92 (each dd, J = 8 & 2 Hz, 1 H), 8.35 & 8.70 (each s, 1 H), 8.37 & 8.44 (each d, J = 2 Hz, 1 H)

IR (Nujol): 1685, 1560, 1305, 1280, 1250, 1135 cm^{-1}

Example 95

1-[N-(6-Chloro-3-pyridylmethyl)-N-formyl]amino-1-dimethylamino-2-nitroethylene (Compound 113)



The reaction procedure of Example 46 was repeated except that 1-N-(6-chloro-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene to give the title compound as pale yellow crystals.

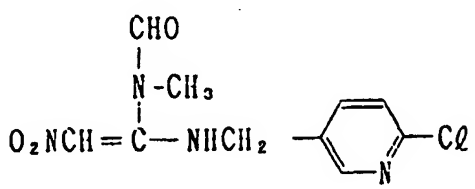
m.p.: 105-106 °C

NMR (DMSO-d_6) δ: 2.93 (s, 6 H), 4.33-5.10 (m, 2 H), 6.72 (s, 1 H), 7.42 (d, J = 8 Hz, 1 H), 7.80 (dd, J = 8 & 2 Hz, 1 H), 8.23 (s, 1 H), 8.36 (d, J = 2 Hz, 1 H)

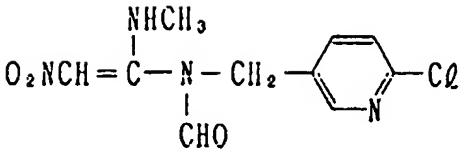
IR (Nujol); 1700, 1565, 1490, 1350, 1270, 1205, 1100 cm^{-1}

Example 96

A 7:3 mixture of 1-(6-chloro-3-pyridylmethyl)-amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 114) and 1-[N-(6-chloro-3-pyridylmethyl)-N-formyl]amino-1-methylamino-2-nitroethylene (Compound 115)



(Compound 114)



(Compound 115)

In 10 ml of DMF was suspended 0.1 g of 60% sodium hydride, previously washed with petroleum ether, and a solution of 0.6 g (0.0025 mole) of 1-N-(6-chloro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene in 5 ml of DMF was added dropwise. The mixture was stirred at room temperature for 1 hour. After cooling, 0.7 g of formic acetic anhydride was added and the mixture was stirred under ice-cooling for 5 hours and, then, at room temperature for 20 hours. The DMF was distilled off under reduced pressure and the residue was diluted with 20 ml of saturated aqueous sodium hydrogen carbonate solution and extracted with CH_2Cl_2 (20 ml x 3). The extract was dried over $MgSO_4$ and the CH_2Cl_2 was distilled off. Finally, the residue was subjected to silica gel column chromatography using EtOH-$CHCl_3$ (1:10) as the eluent. The procedure gave 0.15 g of a 7:3 mixture of the title compounds (Compound 114 and (Compound 115) as white crystals.

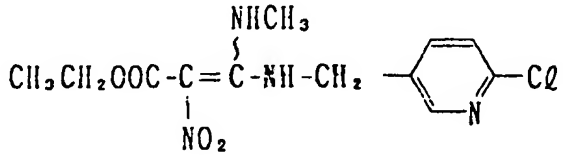
m.p.: 80-85 °C

NMR (DMSO-d_6) δ: (Compound 114) 3.05 (s, 3 H), 4.53 (d, J = 6 Hz, 2 H), 6.76 (s, 1 H), 7.49 (d, J = 8 Hz, 1 H), 7.86 (dd, J = 8 & 2 Hz, 1 H), 8.30 (s, 1 H), 8.42 (d, J = 2 Hz, 1 H), 9.45 (br, 1 H) (Compound 115) 2.95 (d, J = 5 Hz, 3 H), 4.83 (s, 2 H), 6.66 (s, 1 H) , 7.46 (d, J = 8 Hz, 1 H), 7.86 (dd, J = 8 & 2 Hz, 1 H), 8.30 (s, 1 H), 8.42 (d, J = 2 Hz, 1 H), 9.45 (br, 1 H)

IR (Nujol): 3200, 3100, 1685, 1600, 1340, 1250, 1080, 1040 cm^{-1}

Example 97

1-(6-Chloro-3-pyridylmethyl)amino-1-methylamino-2-ethoxycarbonyl-2-nitroethylene (Compound 116)



A mixture of 1.4 g (0.0061 mole) of S-methyl-N-(6-chloro-3-pyridylmethyl)-N'-methylisothiourea obtained in Example 64 (2) and 2.7 g of ethyl nitroacetate was stirred with heating at 75-80 °C for 3 hours. After cooling, the crystals were collected by filtration, washed with CH_3CN and dried. The procedure gave 1.1 g of the title compound as white crystals.

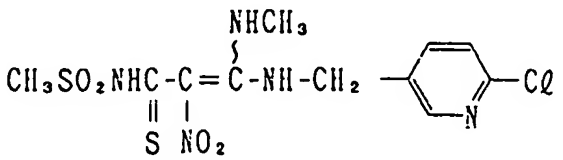
m.p.: 231-233 °C (decompn.)

NMR (DMSO-d_6) δ: 1.07 (3 H, t, J = 7 Hz), 2.86 (3 H, br s), 3.94 (2 H, q, J = 7 Hz), 4.47 (2 H, br s), 7.51 (1 H, d, J = 8 Hz), 7.82 (1 H, dd, J = 8 & 2.7 Hz), 8.38 (1 H, d, J = 2.7 Hz), 9.10-9.60 (2 H, br s)

IR (Nujol): 3250, 1660, 1500, 1320, 1230 cm^{-1}

Example 98

1-(6-Chloro-3-pyridylmethyl)amino-1-methylamino-2-methanesulfonylthiocarbamoyl-2-nitroethylene (Compound 117)



In 50 ml of CH_3CN was dissolved 0.50 g (0.002 mole) of 1-(6-chloro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene, followed by addition of 0.30 g (0.002 mole) of methanesulfonyl isothiocyanate. The mixture was stirred at room temperature for 2 hours. The CH_3CN was distilled off and the residue was purified by silica gel column chromatography. The procedure gave 0.25 g of the title compound as yellow crystals.

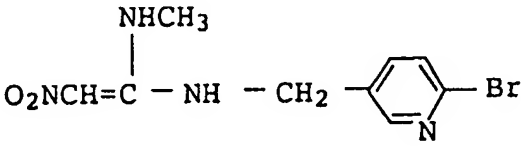
m.p.: 129-131 °C

NMR (DMSO-d_6) δ: 2.76-3.00 (each d, MeN), 3.51 & 3.55 (each s, $MeSO_2$), 4.36-4.70 (each d), 12.20-13.23 (each s)

IR (Nujol): 3200, 1640, 1340, 1140, 920 cm^{-1}

Example 99

1-N-(6-Bromo-3-pyridylmethyl)amino-1-methylamino-2-nitroetylene (Compound 118)



The steps (1), (2) and (3) of Example 13 were repeated except that 6-bromo-3-pyridylmethylamine was used in lieu of N-ethyl-N-(3-pyridylmethyl)amine, to give the following compounds in the respective steps.

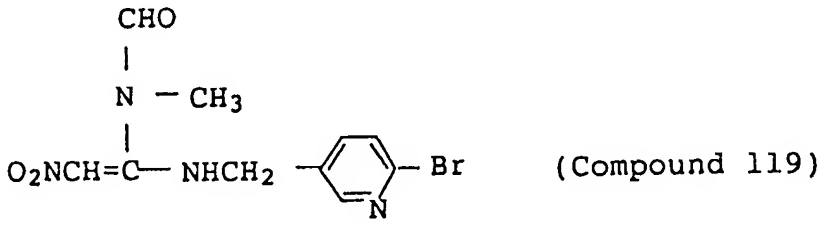
(1) N-(6-Bromo-3-pyridylmethyl)-N'-methylthiourea (white crystals)
(provided that Et_2O-THF (3:1) was used as the reaction solvent)
m.p.: 117-118 °C
NMR(DMSO-d_6)δ: 2.85 (d,J = 5Hz,MeN), 4.67 (d,J = 6Hz,CH_2N), 7.54 (d,J = 8Hz, 1H), 7.6 (br, MeNH), 7.69 (dd, J = 8 & 2 Hz, 1H), 7.93 (t, J = 6Hz,CH_2NH), 8.32 (d,J = 2Hz, 1H)

(2) S-Methyl-N-(6-Bromo-3-pyridylmethyl)-N'-methylisothiourea (yellow oil)
NMR($CDCl_3$)δ: 2.40 (s,MeS), 2.93 (s,MeN =), 4.34(br,NH), 4.47 (S,CH_2N), 7.42 (d,J = 8Hz,1H), 7.61 (dd,J = 8 & 2Hz, 1H), 8.36 (d,J = 2Hz,1H)

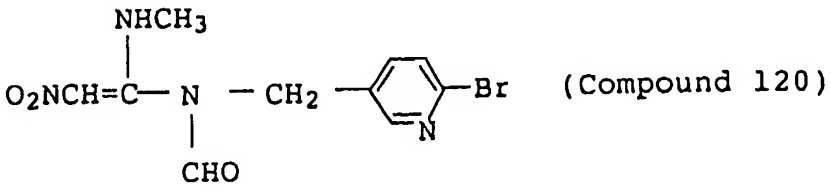
(3) Title compound (pale brown crystals)
m.p.: 184-186 °C (decompn.)
NMR(DMSO-d_6)δ: 2.87 (br.MeN), 4.47 (d,J = 6Hz,CH_2N), 6.46 (s, = $CHNO_2$), 7.61 (d,J = 8Hz,1H), 7.72 (dd,J = 8 & 2Hz,1H), 8.40 (d,J = 2Hz,1H)
IR (Nujol): 1615, 1575, 1455, 1370, 1230, 1200 cm^{-1}

Example 100

1-N-(6-Bromo-3-pyridylmethyl)amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 119) and 1-[N-(6-bromo-3-pyridylmethyl)-N-formyl]amino-1-methylamino-2-nitroethylene (Compound 120)



(Compound 119)



(Compound 120)

The reaction procedure of Example 96 was repeated except that 1-N-(6-bromo-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene was used in lieu of 1-N-(6-chloro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene. To the oil obtained through the purification of silica gel column chromatography, was added a small amount of AcOEt and Et_2O, followed by cooling with dry ice-acetone bath to give a mixture (90:10) of the title compounds (Compound 119 and Compound 120) as pale brown powder. And, the filtrate was concentrated to give a mixture (40:60) of the title compounds (Compound 119 and Compound 120) as viscous product.

(the 90:10 mixture of Compounds 119 and 120)

m.p.: 115-127 °C

NMR(CDCℓ3)δ: (Compound 119) 3.13 (s,MeN), 4.48 (d,J = 6Hz,CH_2N), 6.57 (s, = $CHNO_2$), 7.53 (m,2H,pyridine -H_2), 8.33 (S,2H,CHO and pyridine-H), 9.46 (br,NH)

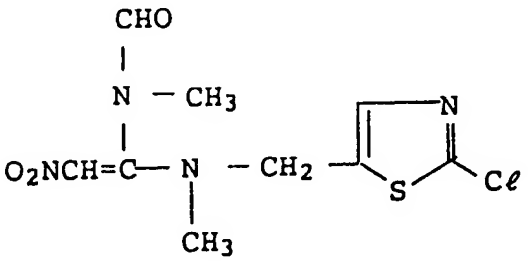
IR (Nujol): 1690, 1620, 1250, 1240, 1080 cm^{-1} (the 40:60 mixture of Compounds 119 and 120)

NMR(CDCℓ3)δ: (Compound 120) 3.01 (d,J = 5Hz,MeN), 4.73 (s,CH_2N), 6.36 (s, = CHNO2), 7.53 (br s,2H,pyridine-H_2),8.34 (br s,2H,CHO and pyridine-H_1), 9.35 (br,NH)

IR (neat): 1680, 1605, 1450, 1350, 1250, 1080 cm^{-1}

Example 101

1-[N-(2-Chloro-5-thiazolylmethyl)-N-methyl)amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 121)



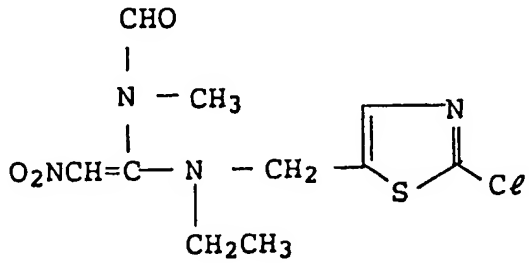
The reaction procedure of Example 46 was repeated except that 1-[N-(2-chloro-5-thiazolylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridyl-methyl)-amino-2-nitroethylene, to give the title compound as pale yellow resinous product.

NMR(DMSO-d_6)δ: 2.92 (s,3H,MeNCH_2), 2.99 (s,3H,MeNCHO), 4.74 (br s,2H,CH_2), 6.90 (s,1H, = $CHNO_2$), 7.71 (s,1H, thiazole-H), 8.19 (s,1H,CHO)

IR (neat): 1695, 1565, 1490, 1340, 1270, 1042 cm^{-1}

Example 102

1-[N-(2-Chloro-5-thiazolylmethyl)-N-ethyl)amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 122)



The reaction procedure of Example 46 was repeated except that 1-[N-(2-chloro-5-thiazolylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridyl-methyl)lamino-2-nitroethylene, to give the title compound as yellow crystals.

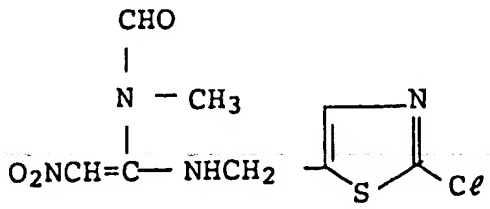
m.p.: 99-100 °C.

NMR(DMSO-dc)δ: 1.15 (t,3H,CH_2CH_3), 2.98 (s,3H,MeN), 3.32 (q,2H,CH_2CH_3), 4.76 (br s,2H,thiazole-CH_2),

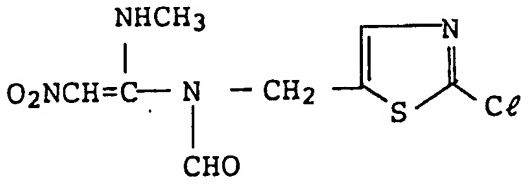
7.02 (s,1H, $=CHNO_2$), 7.72 (s,1H,thiazole-H), 8.17 (s,1H,CHO)
IR (Nujol): 1698, 1577, 1557, 1470, 1448, 1352, 1315, 1270, 1053 cm^{-1}

Example 103

1-N-(2-Chloro-5-thiazolylmethyl)amino-1-[N-formyl-N-methyl)amino-2-nitroethylene (Compound 123) and 1-[N-(2-chloro-5-thiazolylmethyl)-N-formyl]amino-1-methylamino-2-nitroethylene (Compound 124)



(Compound 123)



(Compound 124)

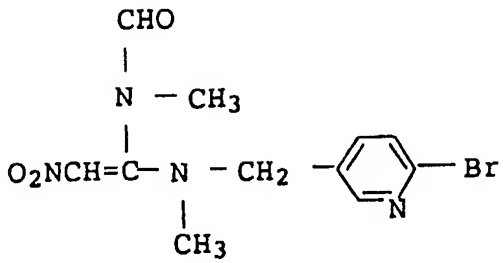
The reaction procedure of Example 100 was repeated except that 1-N-(2-chloro-5-thiazolylmethyl)-amino-1-methylamino-2-nitroethylene was used in lieu of 1-N-(6-bromo-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene, to give the title compound (Compound 124) as crystals and a mixture (70:30) of the title compounds (Compound 123 and Compound 124) as viscous product.

(Compound 124)

m.p.: 125-126 °C
NMR($CDCl_3$)δ: 3.01 (3H,d,J = 6.0 Hz), 4.82 (2H,s), 6.38 (1H,s), 7.49 (1H,s), 8.30 (1H,s), 9.0-9.6 (1H,br)
IR (Nujol): 3220, 1675, 1620, 1245, 1100, 1050 cm^{-1} (the 70:30 mixture of Compounds 123 and 124)
NMR($CDCl_3$)δ: (Compound 123) 3.16 (3H,s), 4.63 (2H,d,J = 5.7 Hz), 6.57 (1H,s), 7.49 (1H,s), 8.35 (1H,s), 9.1-9.6 (1H,br)
IR (neat): 3220, 1680, 1605, 1480, 1250, 1045 cm^{-1}

Example 104

1-[N-(6-Bromo-3-pyridylmethyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 125)

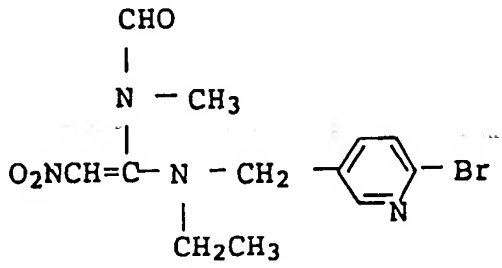


The reaction procedure of Example 46 was repeated except that 1-[N-(6-bromo-3-pyridylmethyl)-N-methyl]amino-1-metylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene, to give the title compound as yellow resinous product.
(provided that THF-DMF was used as the reaction solvent)
NMR($DMSO-d_6$)δ: 2.93 (s,3H), 3.02 (s,3H), 4.3-4.9 (m,2H), 6.87 (s, $=CHNO_2$), 7.68 (br s,2H), 8.23 (s,CHO),

8.3-8.5 (m,1H)
IR (neat): 1685 cm^{-1}

Example 105

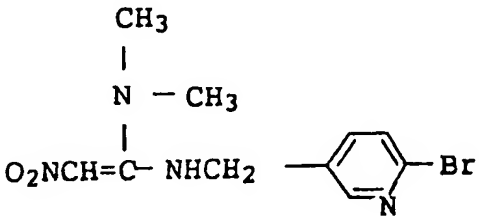
1-[N-(6-Bromo-3-pyridylmethyl)-N-ethyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene (Compound 126)



The reaction procedure of Example 46 was repeated except that 1-[N-(6-bromo-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene, to give the title compound as yellow crystals.
m.p.: 105-108 °C
NMR(DMSO-d_6)δ: 1.13 (t,J = 7.2 Hz,3H), 3.00 (s,3H), 3.1-3.7 (m,2H), 4.3-4.9 (m,2H), 6.97 (s, = $CHNO_2$), 7.5-7.9 (m,2H), 8.21 (s,CHO), 8.38 (br s,1H)
IR (Nujol): 1705 cm^{-1}

Example 106

1-N-(6-Bromo-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene (Compound 127)



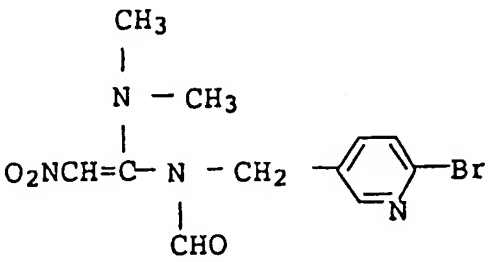
The steps (1), (2), (3) and (4) of Example 88 were repeated except that 6-bromo-3-pyridylmethylamine was used in lieu of 6-chloro-3-pyridylmethylamine, to give the following compounds in the respective steps.

(1) (6-Bromo-3-pyridyl)methyl isothiocyanate (yellow oil)
(provided that after completion of dropwise addition of ethyl chlorocarbonate, the mixture was stirred at 50 °C for 4 hours)
NMR($CDCl_3$)δ: 4.73 (s,2H), 7.43-7.70 (m,2H), 8.35 (br s,1H)
(2) N-(6-Bromo-3-pyridylmethyl)-N'-dimethylthiourea (white crystals)
(provided that the product was purified by silica gel column chromatography using E_tOH-$CHCl_3$ - (1:10) as the eluent)
m.p.: 124-125 °C
NMR($CDCl_3$)δ: 3.27 (s,6H), 4.85 (d,J = 5 Hz,2H), 6.32 (br t,J = 5Hz,1H), 7.40 (d,J = 8Hz,1H), 7.66 (dd,J = 8 & 2 Hz,1H), 8.21 (d,J = 2Hz,1H)
(3) S-Methyl-N-(6-bromo-3-pyridylmethyl)-N'-dimethylisothiourea (yellow oil)
NMR($CDCl_3$)δ: 2.30 (s,3H), 3.00 (s,6H), 4.66 (s,2H), 7.38 (d,J = 8Hz,1H), 7.55 (dd,J = 8 & 2 Hz, 1H), 8.35 (d,J = 2 Hz,1H)
(4) Title compound (pale yellow crystals)
(provided that the reaction was conducted for 20 hours, and the product was purified by silica gel

column chromatography and recrystallized from CH_3CN.
m.p.: 158-159 °C
NMR($CDCl_3$)δ: 2.92 (s,6H), 4.45 (d,J=6 Hz,2H), 6.50 (s,1H), 7.48 (d,J=8 Hz,1H), 7.60 (dd,J=8 & 2 Hz,1H), 8.33 (d,J=2 Hz,1H), 9.70 (br,1H)
IR (Nujol): 3100, 1580, 1550, 1440, 1300, 1260, 1040 cm^{-1}

Example 107

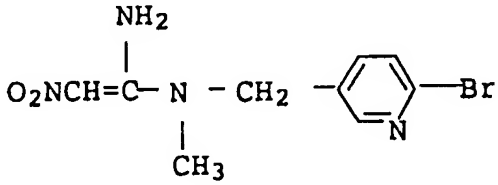
1-[N-(6-Bromo-3-pyridylmethyl)-N-formyl]amino-1-dimethylamino-2-nitroethylene (Compound 128)



The reaction procedure of Example 46 was repeated except that 1-N-(6-bromo-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene, to give the title compound as pale yellow crystals.
(provided that the reaction was conducted in DMF)
m.p.: 96-97 °C
NMR(DMSO-d_6)δ: 2.92 (s,6H), 4.30-5.06 (m,2H), 6.73 (s,1H), 7.50-7.80 (m,2H) 8.23 (s,1H), 8.35 (br s,1H)
IR (Nujol): 1700, 1565, 1490, 1345, 1270, 1080 cm^{-1}

Example 108

1-Amino-1-[N-(6-bromo-3-pyridylmethyl)-N-methyl]amino-2-nitroethylene (Compound 129)



The steps (1) and (2) ofExample 40 were repeated except that N-(6-bromo-3-pyridylmethyl)-N-methylamine was used in lieu of N-(6-chloro-3-pyridylmethyl)-N-ethylamine to give the following compounds in the respective steps.

(1) 1-[N-(6-Bromo-3-pyridylmethyl)-N-methyl]amino-1-methylthio-2-nitroethylene (yellow oil)
(provided that the reaction was conducted for 3.5 hours)
NMR($CDCl_3$)δ: 2.47 (s,3H), 3.03 (s,3H), 4.73 (s,2H), 6.67 (s, 1H), 7.36-7.60 (m,2H), 8.30 (br s,1H)
(2) Title compound (white crystals)
(provided that the reaction was conducted in MeOH for 1 hour, and the precipitated crystals were collected by filtration)
m.p.: 206-207 °C
NMR(DMSO-d_6)δ: 3.03 (s,3H), 4.63 (s,2H), 6.60 (s,1H), 7.43-7.80 (m,2H), 8.30 (br s,1H), 8.88 (br,2H)
IR (Nujol): 3260, 3140, 1620, 1575, 1420, 1290, 1220 cm^{-1}

Example 109

1-N-(2-Chloro-5-thiazolylmethyl)amino-1-dimethylamino-2-nitroethylene (Compound 104)

The steps (1), (2), (3) and (4) of Example 88 were repeated except that 2-chloro-5-thiazolylmethylamine was used in lieu of 6-chloro-3-pyridylmethylamine, to give the following compounds in the respective steps.

(1) (2-Chloro-5-thiazolyl)methyl isothiocyanate

(provided that after completion of dropwise addition of ethyl chlorocarbonate, the mixture was stirred at 80 °C for 3 hours)

NMR($CDCl_3$)δ: 4.82 (2H,s), 7.50 (1H,s)

(2) N-(2-Chloro-5-thiazolylmethyl)-N'-dimethylthiourea (yellow crystals)

m.p.: 125-127 °C

NMR($CDCl_3$)δ: 3.28 (6H,s), 4.98 (2H,d,J = 6.0 Hz), 5.6-6.1 (1H,br), 7.40 (1H,s)

(3) S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N-dimethylisothiourea (yellow oil)

NMR($CDCl_3$)δ: 2.31 (3H,s), 2.99 (6H,s), 4.79 (2H,s), 7.36 (1H,s)

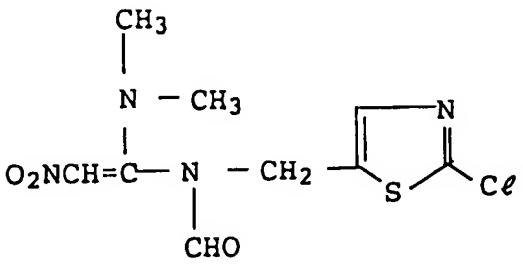
(4) Title compound (pale grey crystals)

(provided that the reaction was conducted for 37 °C)

This product was in agreement with Compound 104 obtained in Example 86 in melting point, NMR and IR spectra and TLC Rf.

Example 110

1-[N-(2-Chloro-5-thiazolylmethyl)-N-formyl]amino-1-dimethylamino-2-nitroethylene (Compound 130)



The reaction procedure of Example 46 was repeated except that 1-N-(2-chloro-5-thiazolylmethyl)amino-1-dimethylamino-2-nitroethylene was used in lieu of 1-methylamino-1-[N-methyl-N-(3-pyridylmethyl)]amino-2-nitroethylene, to give the title compound as white crystals. The NMR value of this product indicated this product was a mixture (6:1) of isomers.

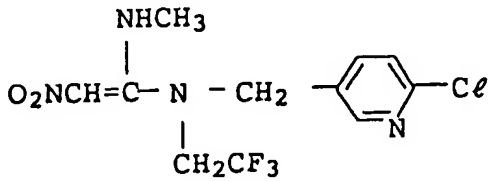
m.p.: 139-142 °C

NMR($CDCl_3$)δ: 2.92 & 2.99 (total 6H, each s), 4.83 (2H,s), 6.61 & 6.34 (total 1H,s), 7.45 (1H,s), 8.19 & 8.46 (total 1H, each s)

IR (Nujol): 1680, 1410, 1355, 1270, 1050 cm^{-1}

Example 111

1-[N-(6-Chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)]amino-1-methylamino-2-nitroethylene (Compound 131)



In 35 mℓ of toluene, 3,79 g (0.0169 mole) of N-(6-chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)amine and 2.46 g of methyl isothiocyanate were stirred for 18 hours under reflux. The toluene was distilled off, and the residue was dissolved in 120 mℓ of AcOEt, washed with 1N HCℓ (two times) and aqueous sodium chloride solution in this order and dried over $MgSO_4$. The AcOEt was distilled off to give oil. To this oily product were added Et_2O and hexane, followed by cooling to give crystals. After addition of hexane to the mixture, the crystals were collected by filtration and dried to give 2.78 g of N-(6-chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)-N'-methylthiourea as white crystals.

m.p.: 98-100 °C

NMR($CDCℓ_3$)δ: 3.13 (d,J = 5 Hz,MeN), 4.37 (q,J = 9 Hz,CF_3CH_2), 5.09 (s,pyridine-CH_2), 6.07 (br,NH), 7.34 (d,J = 8 Hz,1H), 7.67 (dd,J = 8 & 2 Hz,1H), 8.26 (d,J = 2 Hz, 1H)

The steps (2) and (3) of Example 13 were repeated except that N-(6-chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)-N'-methylthiourea was used in lieu of N-methyl-N'-ethyl-N'-(3-pyridylmethyl)thiourea, to give the following compounds in the respective steps.

(2) S-Methyl-N-(6-chloro-3-pyridylmethyl)-N-(2,2,2-trifluoroethyl)-N'-methylisothiourea (pale brown oil)

NMR($CDCℓ_3$)δ: 2.28 (s,MeS), 3.24 (s,MeN), 4.07 (q,J = 9 Hz,CF_3CH_2), 4.66 (s,pyridine-CH_2), 7.28 (d,J = 8 Hz,1H), 7.54 (dd,J = 8 & 2 Hz,1H), 8.26 (d,J = 2 Hz,1H)

(3) Title compound

(provided that the reaction was conducted for 96 hours)

m.p.: 110-111 °C

NMR($CDCℓ_3$)δ: 3.12 (d,J = 5 Hz,MeN), 3.60 (q,J = 9 Hz,CF_3CH_2), 4.42 (s,pyridine-CH_2), 6.51 (s, = $CHNO_2$), 7.39 (d,J = 8 Hz,1H), 7.60 (dd,J = 8 & 2 Hz,1H), 8.33 (d,J = 2 Hz,1H), 9.50 (br,NH)

IR (Nujol): 1595, 1450, 1345, 1260, 1235, 1140, 1100 cm^{-1}

As the object compound (I) of the invention, the following compounds can be synthesized.

(1) 1-[N-(6-Chloro-3-pyridylmethyl)-N-formyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(2) 1-[N-(6-Chloro-3-pyridylmethyl)-N-ethyl]amino-1-dimethylamino-2-nitroethylene
(3) 1-[N-6-Chloro-3-pyridylmethyl)-N-(2-fluoroethyl)]amino-1-methylamino-2-nitroethylene
(4) 1-[N-(6-Chloro-3-pyridylmethyl)-N-(2-fluoroethyl)]amino-1-dimethylamino-2-nitroethylene
(5) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-formyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(6) 1-[N-(6-Bromo-3-pyridylmethyl)-N-(2-fluoroethyl)]amino-1-methylamino-2-nitroethylene
(7) 1-[N-(6-Bromo-3-pyridylmethyl)-N-(2-fluoroethyl)]amino-1-dimethylamino-2-nitroethylene
(8) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-(2-fluoroethyl)]amino-1-methylamino-2-nitroethylene
(9) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-methyl]amino-1-dimethylamino-2-nitroethylene
(10) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-ethyl]amino-1-dimethylamino-2-nitroethylene
(11) 1-(2-Bromo-5-thiazolylmethyl)amino-1-methylamino-2-nitroethylene
(12) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-formyl]amino-1-methylamino-2-nitroethylene
(13) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene
(14) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene
(15) 1-(2-Bromo-5-thiazolylmethyl)amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(16) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-formyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(17) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(18) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-ethyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(19) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-(2-fluoroethyl)]amino-1-dimethylamino-2-nitroethylene
(20) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-formyl]amino-1-dimethylamino-2-nitroethylene
(21) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-methyl]amino-1-dimethylamino-2-nitroethylene
(22) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-ethyl]amino-1-dimethylamino-2-nitroethylene
(23) 1-[N-Chloromethyl-N-(6-chloro-3-pyridylmethyl)]amino-1-methylamino-2-nitroethylene
(24) 1-[N-(6-Bromo-3-pyridylmethyl)-N-chloromethyl]amino-1-methylamino-2-nitroethylene
(25) 1-[N-Chloromethyl-N-(2-chloro-5-thiazolylmethyl)]amino-1-methylamino-2-nitroethylene
(26) 1-[N-(6-Bromo-3-pyridylmethyl)-N-formyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(27) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-(2-fluoroethyl)]amino-1-methylamino-2-nitroethylene
(28) 1-[N-(2-Bromo-5-thiazolylmethyl)-N-(2-fluoroethyl)] amino-1-dimethylamino-2-nitroethylene
(29) 1-[N-(2-Chloro-5-thiazolylmethyl)-N-(2,2,2-trifluoroethyl)]amino-1-methylamino-2-nitroethylene
(30) 1-[N-(6-Bromo-3-pyridylmethyl)-N-(2,2,2-trifluoromethyl)]amino-1-dimethylamino-2-nitroethylene
(31) 1-[N-(6-Bromo-3-pyridylmethyl)-N-methyl]amino-1-dimethylamino-2-nitroethylene
(32) 1-[N-(6-Bromo-3-pyridylmethyl)-N-ethyl]amino-1-dimethylamino-2-nitroethylene
(33) 1-(6-Fluoro-3-pyridylmethyl)amino-1-methylamino-2-nitroethylene
(34) 1-[N-(6-Fluoro-3-pyridylmethyl)-N-formyl]amino-1-methylamino-2-nitroethylene

(35) 1-(6-Fluoro-3-pyridylmethyl)amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(36) 1-[N-(6-Fluoro-3-pyridylmethyl)-N-formyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(37) 1-[N-(6-Fluoro-3-pyridylmethyl)-N-methyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(38) 1-[N-(6-Fluoro-3-pyridylmethyl)-N-ethyl]amino-1-(N-formyl-N-methyl)amino-2-nitroethylene
(39) 1-Dimethylamino-1-(6-fluoro-3-pyridylmethyl)amino-2-nitroethylene
(40) 1-Dimethylamino-1-[N-(6-fluoro-3-pyridylmethyl)-N-formyl]amino-2-nitroethylene
(41) 1-Dimethylamino-1-[N-(6-fluoro-3-pyridylmethyl)-N-methyl]amino-2-nitroethylene
(42) 1-Dimethylamino-1-[N-(6-fluoro-3-pyridylmethyl)-N-ethyl]amino-2-nitroethylene

Example 112 (Emulsifiable concentrate)

An emulsifiable concentrate was manufactured by mixing the following ingredients.

Compound 17	20 weight %
Xylene	75 weight %
Polyoxyethylene glycol ether (Nonipol 85®)	5 weight %

Example 113 (Wettable powder)

A wettable powder was manufactured by mixing the following ingredients.

Compound 12	20 weight %
Sodium ligninsulfonate	5 weight %
Polyoxyethylene glycol ether (Nonipol 85®)	5 weight %
White carbon	30 weight %
Clay	40 weight %

Example 114 (Dust)

A dust was manufactured by mixing the following ingredients.

Compound 19	3 weight %
White carbon	3 weight %
Clay	94 weight %

Example 115 (Granules)

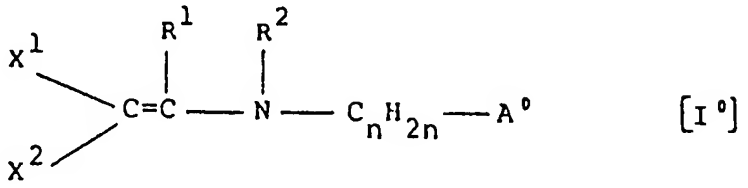
A granular product was prepared by admixing and granulating the following components.

Compound 25	2 weight %
Sodium ligninsulfonate	5 weight %
Clay	93 weight %

Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

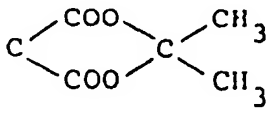
1. An α-unsaturated amine of the formula:



[I⁰]

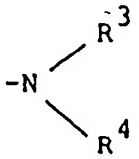
wherein:

one of X^1 and X^2 is an electron-attracting group and the other is a hydrogen atom or an electron-attracting group, wherein the said electron-attracting group is cyano, nitro, C_{1-4} alkoxy carbonyl, carboxyl, C_{6-10} aryloxy-carbonyl, heterocycleoxycarbonyl, C_{1-4} alkylsulfonyl which may be substituted with halogen, aminosulfonyl, di-C_{1-4} alkoxyphosphoryl, C_{1-4} alkanoyl which may be substituted with halogen, C_{1-4} alkylsulfonylthiocarbamoyl, carbamoyl or halogen, or X^1 and X^2 together with the carbon atom to which they are attached form a ring of the formula:



;

R^1 is a group of the formula:

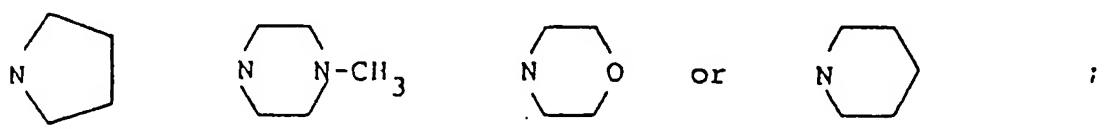


in which:

R^3 is hydrogen, C_{1-20} alkyl, C_{6-10} aryl, C_{7-9} aralkyl, heterocycle, C_{1-4} alkanoyl, C_{6-10} aryl-carbonyl, C_{1-4} alkoxy-carbonyl, C_{6-10} aryloxy-carbonyl, heterocycleoxycarbonyl, C_{6-10} arylsulfonyl, C_{1-4} alkylsulfonyl, di-C_{1-4} alkoxyphosphoryl, C_{1-4} alkoxy, hydroxy, amino, di-C_{1-4} alkylamino, C_{1-4} alkanoylamino, C_{1-4} alkoxycarbonylamino, C_{1-4} alkylsulfonylamino, di-C_{1-4} alkoxyphosphorylamino, C_{7-9} aralkyloxy or C_{1-4} alkoxy-carbonyl-C_{1-4} alkyl; and

R^4 is hydrogen, C_{1-20} alkyl, C_{3-6} cycloalkyl, C_{2-6}-alkenyl, C_{3-6} cycloalkenyl or C_{2-6} alkynyl, wherein each of the radicals defined for R^4 except for hydrogen may optionally be substituted by 1 to 3 substituents selected from the group consisting of hydroxy, C_{1-4} alkoxy, halogen, di-C_{1-4} alkylamino, C_{1-4} alkylthio, C_{1-3} alkanoylamino, C_{1-4} alkylsulfonylamino, tri-C_{1-4} alkylsilyl, pyridyl and thiazolyl, and each of the pyridyl and thiazolyl may further be substituted by halogen, or

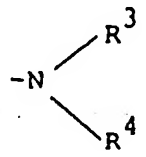
R^3 and R^4 together with the adjacent nitrogen atom constitute a cyclic amino group of the formula:



;

R^2 is (1) hydrogen, (2) a group attached through a carbon atom selected from the class consisting of C_{1-4} alkanoyl, C_{1-20} alkyl, C_{2-6} alkenyl, C_{3-6} cycloalkyl, C_{6-10} aryl, C_{7-9} aralkyl and 3- or 4-

pyridyl, the said group attached through a carbon atom being optionally substituted by 1 to 3 substituents selected from the class consisting of C_{1-4} alkylthio, C_{1-4} alkoxy, mono- or di-C_{1-4} alkylamino, C_{1-4} alkoxy-carbonyl, C_{1-4} alkylsulfonyl, halogen and C_{1-4} alkanoyl, (3) a group attached through an oxygen atom selected from the class consisting of C_{1-4} alkoxy, C_{3-6} cycloalkoxy, C_{2-4} alkenyloxy, C_{3-6} cycloalkenyloxy, ethynyloxy, C_{6-10} aryloxy, thienyloxy and hydroxy, the said group attached through an oxygen atom being optionally substituted by 1 to 3 substituents selected from the class consisting of halogen and phenyl, or (4) a group attached through a nitrogen atom of the formula:



wherein

R^3 and R^4 have the meanings given above;

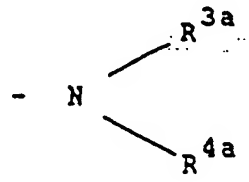
n is an integer of 0, 1 or 2;

$\bar{A}^{\circ}$ is heterocycle;

wherein the heterocycle in the said heterocycle carbonyl for X^1 and X^2, the said heterocycle for R^3, the heterocycle in the said heterocycleoxycarbonyl for R^3,
and the said heterocycle for A° are a member selected from the class consisting of thienyl, furyl, pyrrolyl, pyridyl, oxazolyl, thiazolyl, pyrazolyl, imidazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, N-oxidopyridyl, pyrimidinyl, N-oxidopyrimidinyl, pyridazinyl, pyrazinyl, N-oxidopyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazo[1,5-b]-pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl and phenoxazinyl, the said heterocycle being optionally substituted by 1 to 5 substituents selected from the group consisting of:

(i) C_{1-4} alkyl,
(ii) C_{3-6} cycloalkyl,
(iii) C_{6-10} aryl,
(iv) C_{1-4} alkoxy,
(v) C_{3-6} cycloalkyloxy,
(vi) C_{6-10} aryloxy,
(vii) C_{7-12} aralkyloxy
(viii) C_{1-4} alkylthio,
(ix) C_{3-6} cycloalkylthio,
(x) C_{6-10} arylthio,
(xi) C_{7-12} aralkylthio,
(xii) mono-C_{1-4} alkylamino,
(xiii) di-C_{1-4} alkylamino,
(xiv) C_{3-6} cycloalkylamino,
(xv) C_{6-10} arylamino,
(xvi) C_{7-12} aralkylamino,
(xvii) halogen,
(xviii) C_{1-4} alkoxycarbonyl,
(xix) C_{6-10} aryloxycarbonyl,
(xx) C_{3-6} cycloalkyloxycarbonyl,
(xxi) C_{7-12} aralkyloxycarbonyl,
(xxii) C_{1-5} alkanoyl,
(xxiii) C_{1-15} alkanoyloxy,
(xxiv) carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-ethylcarbamoyl, N,N-diethylcarbamoyl N-phenylcarbamoyl, pyrrolidinocarbamoyl, piperidinocarbamoyl, piperazinocarbamoyl, morpholinocarbamoyl or N-benzylcarbamoyl,

(xxv) N-methylcarbamoyloxy, N,N-dimethylcarbamoyloxy, N-ethylcarbamoyloxy, N-benzylcarbamoyloxy, N,N-dibenzylcarbamoyloxy or N-phenylcarbamoyloxy,
(xxvi) C_{1-4} alkanoylamino,
(xxvii) C_{6-10} arylcarbonylamino,
(xxviii) C_{1-4} alkoxycarbonylamino,
(xxix) C_{7-12} aralkyloxycarbonyl,
(xxx) methanesulfonylamino, ethanesulfonylamino, butanesulfonylamino, benzenesulfonylamino, toluenesulfonylamino, naphthalenesulfonylamino, trifluoromethanesulfonylamino, 2-chloroethanesulfonylamino or 2,2,2-trifluoromethanesulfonylamino,
(xxxi) pyrrolidinyl, pyrrolyl, pyrazolyl, imidazolyl, furyl, thienyl, oxazolyl, isoxazolyl, isothiazolyl, thiazolyl, piperidinyl, pyridyl, piperazinyl, pyrimidinyl, pyranyl, tetrahydropyranyl, tetrahydrofuryl, indolyl, quinolyl, 1,3,4-oxadiazolyl, thieno[2,3-d]pyridyl, 1,2,3-thiadiazolyl, 1,3,4-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1,3,4-triazolyl, tetrazolyl, 4,5-dihydro-1,3-dioxazolyl, tetrazolo[1,5-b]-pyridazinyl, benzothiazolyl, benzoxazolyl, benzimidazolyl or benzothienyl,
(xxxii) heterocyclethio, heterocycleoxy, heterocycleamino or heterocyclecarbonylamino group which is derived by attachment of any of the heterocyclic groups (xxxi) defined above to the S, O, N atom or a carbonylamino group,
(xxxiii) di-C_{1-4} alkylphosphinothioylamino,
(xxxiv) methoxyimino, ethoxyimino, 2-fluoroethoxyimino, carboxymethoxyimino, 1-carboxy-1-methylethoxyimino, 2,2,2-trichloroethoxycarbonylmethoxyimino, 1-(2,2,2-trichloroethoxycarbonyl)-1-methylethoxyimino, (2-aminothiazol-4-yl)methoxyimino or (1H-imidazol-4-yl)methoxyimino,
(xxxv) C_{1-4} alkylsulfonyloxy,
(xxxvi) C_{6-10} arylsulfonyloxy,
(xxxvii) di-C_{6-10} arylphosphino-thioylamino,
(xxxviii) thiocarbamoylthio, N-methylthiocarbamoylthio, N,N-dimethylthiocarbamoylthio, N-ethylthiocarbamoylthio, N-benzylthiocarbamoylthio, N,N-dibenzylthiocarbamoylthio or N-phenylthiocarbamoylthio,
(xxxix) trimethylsilyloxy, t-butyldimethylsilyloxy, t-butyldiphenylsilyloxy or dimethylphenylsilyloxy,
(xL) trimethylsilyl, t-butyldimethylsilyl, t-butyldiphenylsilyl or dimethylphenylsilyl,
(xLi) C_{1-4} alkylsulfinyl,
(xLii) C_{6-10} arylsulfinyl,
(xLiii) C_{1-4} alkylsulfonyl,
(xLiv) C_{6-10} arylsulfonyl,
(xLv) C_{1-4} alkoxy-carbonyloxy,
(xLvi) halo-C_{1-4} alkyl,
(xLvii) halo-C_{1-4} alkoxy, halo-C_{1-4} alkylthio, halo-C_{1-4} alkylsulfinyl or halo-C_{1-4} alkylsulfonyl,
(xLviii) cyano, nitro, hydroxyl, carboxyl, sulfo, phosphono,
(xLix) C_{1-4} alkyloxysulfonyl,
(L) C_{6-10} aryloxysulfonyl,
(Li) C_{7-12} aralkyloxysulfonyl, and
(Lii) di-C_{1-4} alkyloxyphosphoryl group, with the proviso that when R^2 is a hydrogen atom, R^1 is a group of the formula:



[wherein R^{3a} is hydrogen, C_{1-4} alkyl, C_{7-9} phenylalkyl or C_{1-4} alkanoyl and R^{4a} is a hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy-C_{1-4} alkyl, (di-C_{1-4} alkylamino)-C_{1-4} alkyl, tri-C_{1-4} alkylsilyl-C_{1-4} alkyl, C_{2-4} alkenyl or pyridyl- or thiazolyl-C_{1-2} alkyl wherein pyridyl or thiazolyl moiety may optionally be substituted with a halogen atom, or R^{3a} and R^{4a} taken together with the adjacent nitrogen atom constitute pyrrolidino) and A^o is pyridyl, pyrazinyl or thiazolyl, each of which may optionally be substituted with a halogen, C_{1-4} alkyl, C_{1-4} alkylthio or C_{1-4} alkoxy),
and with the proviso that when

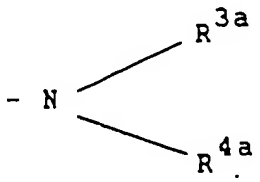
$$\begin{matrix} X^1 \\ X^2 \end{matrix} > C =$$

is O_2N-CH=;
R^1 is

$$-\underset{\underset{R^4}{|}}{N}-R^3 \quad ;$$

R^3 is hydrogen, C_{1-5} alkyl or C_{3-6} cycloalkyl;
R^4 is hydrogen, C_{1-5} alkyl, C_{3-6} cycloalkyl, benzyl or pyrimidinylmethyl; or
R^3 and R^4 together with the adjacent nitrogen atom constitute a cyclic amino group of pyrrolidinyl or piperazinyl; and
R^2 is hydrogen, C_{1-5} alkyl or C_{3-6} cycloalkyl,
A^0 is not a pyridyl subsituted by C_{1-4} haloalkyl, C_{1-4} haloalkoxy, C_{1-4} haloalkylthio, C_{1-4} haloalkylsulfinyl, C_{1-4} haloalkylsulfonyl, cyano, nitro or hydroxyl,
or a salt thereof.

2. A compound as claimed in claim 1, wherein R^2 is hydrogen, R^1 is a group of the formula:



(wherein R^{3a} and R^{4a} are as defined in claim 1) and A^0 is heterocycle selected from the class consisting of pyridyl, pyrazinyl and thiazolyl, the said heterocycle mentioned just above for A^0 being optionally substituted with halogen, C_{1-4} alkyl, C_{1-4} alkylthio or C_{1-4} alkoxy.

3. A compound as claimed in claim 1, wherein R^2 is other than hydrogen.

4. A compound as claimed in claim 1, wherein,
X^1 is nitro;
X^2 is hydrogen, C_{1-2} alkoxycarbonyl or C_{1-2} alkylsulfonylthiocarbamoyl;
R^1 is amino, mono- or di-C_{1-4} alkylamino, halo-C_{1-4} alkylamino, N-C_{1-4} alkyl-N-C_{1-2} alkanoylamino, N-halo-C_{1-4} alkyl-N-C_{1-2} alkanoylamino or C_{1-2} alkanoylamino;
R^2 is hydrogen, C_{1-2} alkoxy, di-C_{1-2} alkylamino, C_{1-4} alkyl, halo-C_{1-4} alkyl or C_{1-2} alkanoyl;
n is 0 or 1;
A^0 is 2- or 3-thienyl, 2- or 3-furyl, 2- or 3-pyrrolyl, 2-, 3- or 4-pyridyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxido-2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxido-2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxido-3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]-pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl or phenoxyazinyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl, halo-C_{1-4} alkyl, C_{1-4} alkoxy, halo-C_{1-4} alkoxy, C_{1-4} alkylthio or halo-C_{1-4} alkylthio or a salt thereof.

5. A compound as claimed in claim 1, wherein,

X^1 is nitro;

X^2 is hydrogen or C_{1-2} alkylsulfonylthiocarbamoyl;

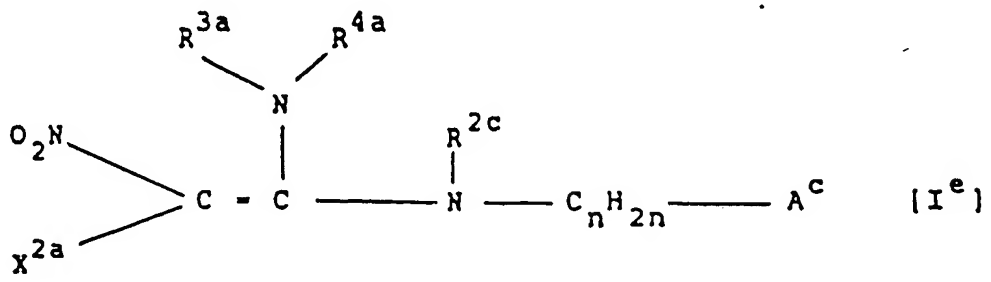
R^1 is amino, mono- or di-C_{1-2} alkylamino, halo-C_{1-2} alkylamino, N-C_{1-2} alkyl-N-C_{1-2} alkanoylamino, N-halo-C_{1-2} alkyl-N-C_{1-2} alkanoylamino or C_{1-2} alkanoylamino;

R^2 is hydrogen, C_{1-2} alkoxy, di-C_{1-2} alkylamino, C_{1-4} alkyl, halo-C_{1-4} alkyl or C_{1-2} alkanoyl;

n is 1; and

A^o is pyridyl, pyrazinyl or thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl, halo-C_{1-4} alkyl, C_{1-4} alkoxy, halo-C_{1-4} alkoxy, C_{1-4} alkylthio or halo-C_{1-4} alkylthio or a salt thereof.

6. A compound as claimed in claim 1, of the formula



[I^e]

wherein:

X^{2a} is hydrogen, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl;

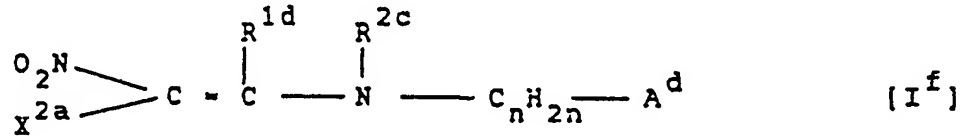
R^{2c} is hydrogen, C_{1-3} alkanoyl, C_{1-4} alkyl, mono- or di-C_{1-4} alkoxy-C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di-C_{1-4} alkylamino or C_{1-4} alkoxy;

A^c is 3- or 4-pyridyl, pyrazinyl or 4- or 5-thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy;

n is 1; and

R^{3a} and R^{4a} are as defined in claim 1 , or a salt thereof.

7. A compound as claimed in claim 1, which is a compound of the formula:



[I^f]

wherein:

X^{2a} is hydrogen, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl;

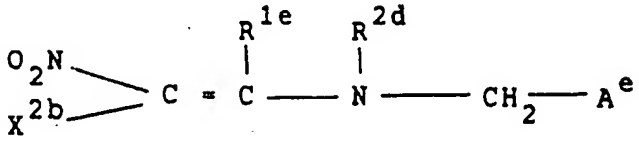
R^{1d} is amino, mono- or di-C_{1-4} alkylamino, N-C_{1-4} alkyl-N-C_{1-3} alkanoylamino C_{7-9} aralkylamino, halogenothiazolyl-C_{1-2} alkylamino or C_{1-4} alkoxy-C_{1-2} alkylamino;

R^{2c} is hydrogen, C_{1-3} alkanoyl, C_{1-4} alkyl, mono- or di-C_{1-4} alkoxy-C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di-C_{1-4} alkylamino or C_{1-4} alkoxy;

n is 0, 1 or 2; and

A^d is 3- or 4-pyridyl, pyrazinyl or 5-thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy, or a salt thereof.

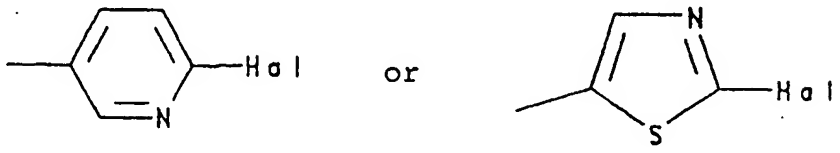
8. A compound as claimed in claim 1, which is a compound of the formula:



[I^g]

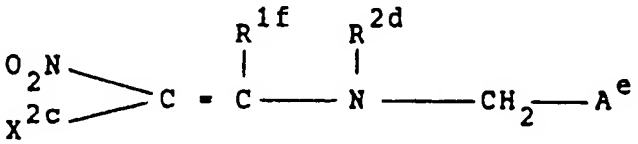
wherein:

X^{2b} is hydrogen or C_{1-2} alkylsulfonylthiocarbamoyl;
R^{1e} is amino, mono- or di-C_{1-2} alkylamino or N-C_{1-2} alkyl-N-formylamino;
R^{2d} is hydrogen, C_{1-2} alkyl or C_{1-3} alkanoyl; and
A^e is a group of the formula:



wherein Hal is a halogen atom, or a salt thereof.

9. A compound as claimed in claim 1, which is a compound of the formula:



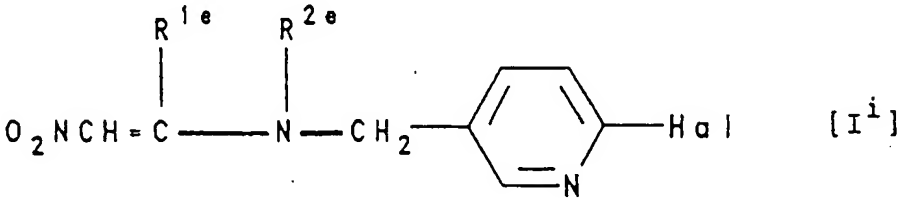
[I^h]

wherein:

X^{2c} is hydrogen or methylsulfonylthiocarbamoyl;
R^{1f} is amino, methylamino, dimethylamino or N-methyl-N-formylamino;
R^{2d} is a hydrogen atom, formyl or C_{1-2} alkyl; and
A^e is a group of the formula:

wherein Hal is a halogen atom, or a salt thereof.

10. A compound as claimed in claim 1, which is a compound of the formula:



[I^i]

wherein:

R^{1e} is amino, mono- or di-C_{1-2} alkylamino or N-C_{1-2} alkyl-N-formylamino;

R^{2e} is C_{1-2} alkyl or formyl; and

Hal is a halogen atom, or a salt thereof.

11. A compound as claimed in claim 1, wherein the heterocycle is selected from the following group and being optionally substituted as defined in claim 1, the group consisting of 2- or 3-thienyl, 2- or 3-furyl, 2- or 3- pyrrolyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxido-2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxido-2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxido-3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]pyridazinyl, triszolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl and phenoxazinyl.

12. A compound as claimed in claim 1, selected from 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene, 1-(6-chloro-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene, and 1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene.

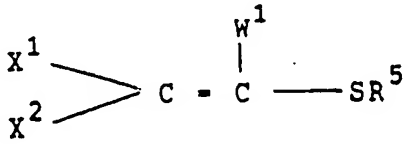
13. An insecticidal/miticidal composition which comprises an insecticidal/miticidal effective amount of at least one of the α-unsaturated amines as claimed in any one of claims 1 to 12, or a salt thereof, together with a suitable carrier or carriers.

14. A process for preparing an α-unsaturated amine of the formula:

[I^o]

wherein the symbols are as defined in claim 1 or a salt thereof, which comprises

(1) reacting a compound of the formula:

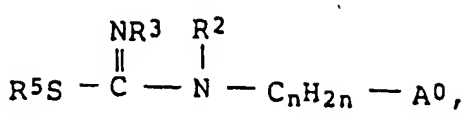


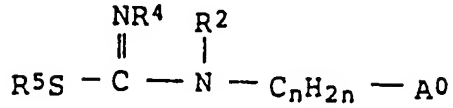
or a salt thereof with a compound of the formula:

Y - W^2

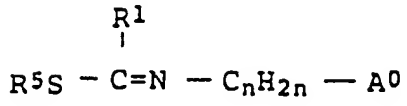
or a salt thereof, or

(2) reacting a compound of the formula:

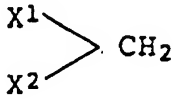




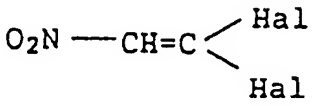
or



or a salt thereof with a compound of the formula:



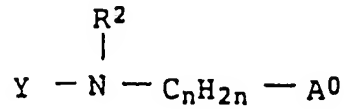
or a salt thereof, or
(3) reacting a compound of the formula:



or

$O_2N - CH_2C(Hal)_3$

(i) with a compound of the formula:



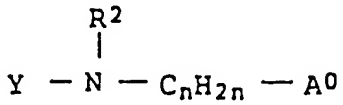
or a salt thereof, and then reacting the resulting product with a compound of the formula:

$R^1 - Y$

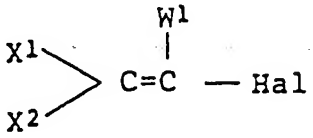
or a salt thereof, or (ii) with a compound of the formula:

$R^1 - Y$

or a salt thereof, and then reacting the resulting product with a compound of the formula:



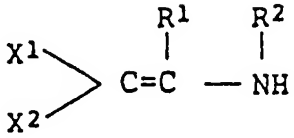
or a salt thereof, or
(4) reacting a compound of the formula:



or a salt thereof with a compound of the formula:

$Y - W^2$

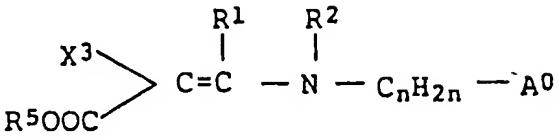
or a salt thereof, or
(5) reacting a compound of the formula:



or a salt thereof with a compound of the formula:

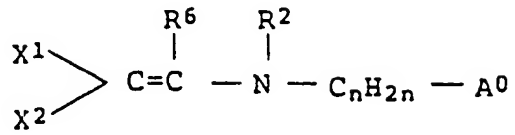
$A^0 - C_nH_{2n} - Hal$

or a salt thereof, or
(6) subjecting a compound of the formula:

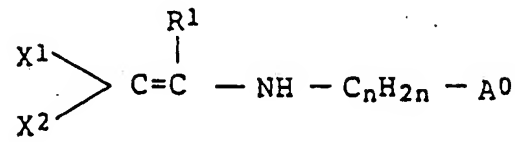


or a salt thereof to hydrolysis reaction and then to decarboxylation reaction, or

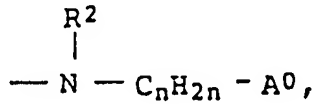
(7) subjecting a compound of the formula:



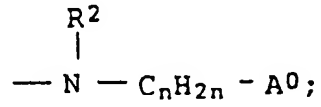
or



or a salt thereof to alkylation, acylation, alkoxycarbonylation, sulfonylation or phosphorylation, in which formulas, R^5 is a C_{1-4} alkyl or aralkyl; when W^1 is



W^2 is R^1 and when W^1 is R^1, W^2 is



Y is a hydrogen atom or an alkali metal;
R^3 is a hydrogen atom, alkyl, aryl aralkyl, heterocyclic, acyl, alkoxycarbonyl, aryloxycarbonyl, heterocycleoxycarbonyl, arylsulfonyl, alkylsulfonyl, dialkoxyphosphoryl, alkoxy, hydroxyl, amino, dialkylamino, acylamino, alkoxycarbonylamino, alkylsulfonylamino, dialkoxyphosphorylamino, aralkyloxy or alkoxycarbonylalkyl; R^4 is a hydrogen atom, or alkyl, cycloalkyl, alkenyl, cycloalkenyl or alkynyl which groups may optionally be substituted, or pyridyl- or thiazolyl-C_{1-2} alkyl wherein pyridyl and thiazolyl moiety may optionally be substituted with a halogen atom; Hal is a halogen atom;
X^3 is an electron-attracting group; R^5 is a group attached through a nitrogen atom containing at least one hydrogen atom; and X^1, X^2, R^1, R^2, n and A^0 are as defined in claim 1.

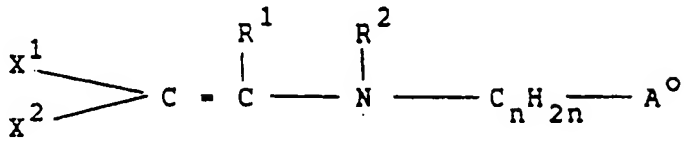
15. A method of combatting undesirable insects or mites, which comprises applying an insecticidal or miticidal effective amount of the compound of the formula [I°] defined in any one of claims 1 to 12 or a salt thereof to the said insects or mites or their habitat.

16. A method of claim 15, wherein the compound or salt is applied in a composition of the compound or salt with a suitable carrier or carriers.

17. A method of combatting undesirable insects or mites, which comprises applying an insecticidal or miticidal effective amount of the compound of the formula [I°] defined in claim 12.

Claims for the following Contracting State : ES

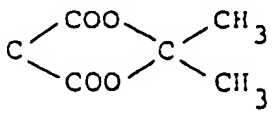
1. A process for preparing an α-unsaturated amine of the formula:



[I°]

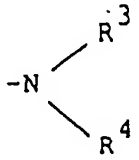
wherein:

one or X^1 and X^2 is an electron-attracting group and the other is a hydrogen atom or an electron-attracting group, wherein the said electron-attracting group is cyano, nitro, C_{1-4} alkoxy carbonyl, carboxyl, C_{6-10} aryloxy-carbonyl, heterocycleoxycarbonyl, C_{1-4} alkylsulfonyl which may be substituted with halogen, aminosulfonyl, di-C_{1-4} alkoxyphosophoryl, C_{1-4} alkanoyl which may be substituted with halogen, C_{1-4} alkylsulfonylthiocarbamoyl, carbamoyl or halogen, or X^1 and X^2 together with the carbon atom to which they are attached form a ring of the formula:



;

R^1 is a group of the formula:

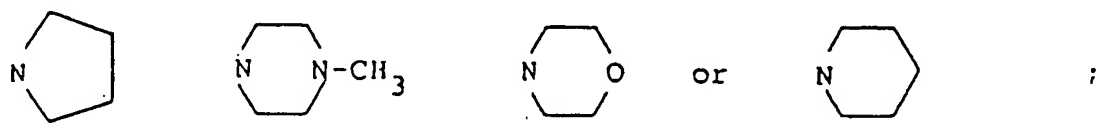


in which:

R^3 is hydrogen, C_{1-20} alkyl, C_{6-10} aryl, C_{7-9} aralkyl, heterocycle, C_{1-4} alkanoyl, C_{6-10} aryl-carbonyl, C_{1-4} alkoxy-carbonyl, C_{6-10} aryloxy-carbonyl, heterocycleoxycarbonyl, C_{6-10} arylsulfonyl, C_{1-4} alkylsulfonyl, di-C_{1-4} alkoxyphosphoryl, C_{1-4} alkoxy, hydroxy, amino, di-C_{1-4} alkylamino, C_{1-4} alkanoylamino, C_{1-4} alkoxycarbonylamino, C_{1-4} alkylsulfonylamino, di-C_{1-4} alkoxyphosphorylamino, C_{7-9} aralkyloxy or C_{1-4} alkoxy-carbonyl-C_{1-4} alkyl; and

R^4 is hydrogen, C_{1-20} alkyl, C_{3-6} cycloalkyl, C_{2-6}-alkenyl, C_{3-6} cycloalkenyl or C_{2-6} alkynyl, wherein each of the radicals defined for R^4 except for hydrogen may optionally be substituted by 1 to 3 substituents selected from the group consisting of hydroxy, C_{1-4} alkoxy, lialogen, di-C_{1-4} alkylamino, C_{1-4} alkylthio, C_{1-3} alkanoylamino, C_{1-4} alkylsulfonylamino, tri-C_{1-4} alkylsilyl, pyridyl and thiazolyl, and each of the pyridyl and thiazolyl may further be substituted by halogen, or

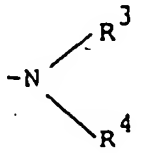
R^3 and R^4 together with the adjacent nitrogen atom constitute a cyclic amino group of the formula:



;

R^2 is (1) hydrogen, (2) a group attached through a carbon atom selected from the class consisting of C_{1-4} alkanoyl, C_{1-20} alkyl, C_{2-6} alkenyl, C_{3-6} cycloalkyl, C_{6-10} aryl, C_{7-9} aralkyl and 3- or 4-pyridyl, the said group attached through a carbon atom being optionally substituted by 1 to 3 substituents selected from the class consisting of C_{1-4} alkylthio, C_{1-4} alkoxy, mono-or di-C_{1-4} alkylamino, C_{1-4} alkoxy-carbonyl, C_{1-4} alkylsulfonyl, halogen and C_{1-4} alkanoyl, (3) a group attached

through an oxygen atom selected from the class consisting of C_{1-4} alkoxy, C_{3-6} cycloalkoxy, C_{2-4} alkenyloxy, C_{3-6} cycloalkenyloxy, ethynyloxy, C_{6-10} aryloxy, thienyloxy and hydroxy, the said group attached through an oxyyen atom being optionally substituted by 1 to 3 substituents selected from the class consisting of halogen and phenyl, or (4) a group attached through a nitrogen atom of the formula:



wherein R^3 and R^4 have the meanings given above;

n is an integer of 0, 1 or 2;

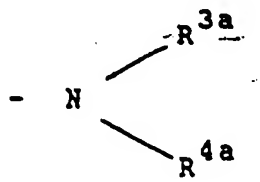
$\bar{A}^o$ is heterocycle,

wherein the heterocycle in the said heterocycle carbonyl for X^1 and X^2, the said heterocycle for R^3, the heterocycle in the said heterocycleoxycarbonyl for R^3,

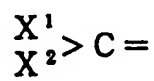
and the said heterocycle for A^o are a member selected from the class consisting of thienyl, furyl, pyrrolyl, pyridyl, oxazolyl, thiazolyl, pyrazolyl, imidazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, N-oxidopyridyl, pyrimidinyl, N-oxidopyrimidinyl, pyridazinyl, pyrazinyl, N-oxidopyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazo[1,5-b]-pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl and phenoxazinyl, the said heterocycle being optionally substituted by 1 to 5 substituents selected from the group consisting of,

(i) C_{1-4} alkyl,
(ii) C_{3-6} cycloalkyl,
(iii) C_{6-10} aryl,
(iv) C_{1-4} alkoxy,
(v) C_{3-6} cycloalkyloxy,
(vi) C_{6-10} aryloxy,
(vii) C_{7-12} aralkyloxy
(viii) C_{1-4} alkylthio,
(ix) C_{3-6} cycloalkylthio,
(x) C_{6-10} arylthio,
(xi) C_{7-12} aralkylthio,
(xii) mono-C_{1-4} alkylamino,
(xiii) di-C_{1-4} alkylamino,
(xiv) C_{3-6} cycloalkylamino,
(xv) C_{6-10} arylamino,
(xvi) C_{7-12} aralkylamino,
(xvii) halogen,
(xviii) C_{1-4} alkoxycarbonyl,
(xix) C_{6-10} aryloxycarbonyl,
(xx) C_{3-6} cycloalkyloxycarbonyl,
(xxi) C_{7-12} aralkyloxycarbonyl,
(xxii) C_{1-5} alkanoyl,
(xxiii) C_{1-15} alkanoyloxy,
(xxiv) carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-ethylcarbamoyl, N,N-diethylcarbamoyl N-phenylcarbamoyl, pyrrolidinocarbamoyl, piperidinocarbamoyl, piperazinocarbamoyl, morpholinocarbamoyl or N-benzylcarbarmoyl,
(xxv) N-methylcarbamoyloxy, N,N-dimethylcarbamoyloxy, N-ethylcarbamoyloxy, N-benzylcarbamoyloxy, N,N-dibenzylcarbamoyloxy or N-phenylcarbamoyloxy,
(xxvi) C_{1-4} alkanoylamino,
(xxvii) C_{6-10} arylcarbonylamino,
(xxviii) C_{1-4} alkoxycarbonylamino,

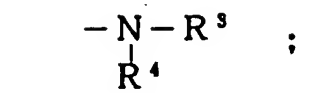
(xxix) C_{7-12} aralkyloxycarbonyl,
(xxx) methanesulfonylamino, ethanesulfonylamino, butanesulfonylamino, benzenesulfonylamino, toluenesulfonylamino, naphthalenesulfonylamino, trifluoromethanesulfonylamino, 2-chloroethanesulfonylamino or 2,2,2-trifluoromethanesulfonylamino,
(xxxi) pyrrolidinyl, pyrrolyl, pyrazolyl, imidazolyl, furyl, thienyl, oxazolyl, isoxazolyl, isothiazolyl, thiazolyl, piperidinyl, pyridyl, piperazinyl, pyrimidinyl, pyranyl, tetrahydropyranyl, tetrahydrofuryl, indolyl, quinolyl, 1,3,4-oxadiazolyl, thieno[2,3-d]pyridyl, 1,2,3-thiadiazolyl, 1,3,4-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1,3,4-triazolyl, tetrazolyl, 4,5-dihydro-1,3-dioxazolyl, tetrazolo[1,5-b]-pyridazinyl, benzothiazolyl, benzoxazolyl, benzimidazolyl or benzothienyl,
(xxxii) heterocyclethio, heterocycleoxy, heterocycleamino or heterocyclecarbonylamino group which is derived by attachment of any of the heterocyclic groups (xxxi) defined above to the S, O, N atom or a carbonylamino group,
(xxxiii) di-C_{1-4} alkylphosphinothioylamino,
(xxxiv) methoxyimino, ethoxyimino, 2-fluoroethoxyimino, carboxymethoxyimino, 1-carboxy-1-methylethoxyimino, 2,2,2-trichloroethoxycarbonylmethoxyimino, 1-(2,2,2-trichloroethoxycarbonyl)-1-methylethoxyimino, (2-aminothiazol-4-yl)methoxylmino or (1H-imidazol-4-yl)methoxyimino,
(xxxv) C_{1-4} alkylsulfonyloxy,
(xxxvi) C_{6-10} arylsulfonyloxy,
(xxxvii) di-C_{6-10} arylphosphino-thioylamino,
(xxxviii) thiocarbamoylthio, N-methylthiocarbamoylthio, N,N-dimethylthiocarbamoylthio, N-ethylthiocarbamoylthio, N-benzylthiocarbamoylthio, N,N-dibenzylthiocarbamoylthio or N-phenylthiocarbamoylthio,
(xxxix) trimethylsilyloxy, t-butyldimethylsilyloxy, t-butyldiphenylsilyloxy or dimethylphenylsilyloxy,
(xL) trimethylsilyl, t-butyldimethylsilyl, t-butyldiphenylsilyl or dimethylphenylsilyl,
(xLi) C_{1-4} alkylsulfinyl,
(xLii) C_{6-10} arylsulfinyl,
(xLiii) C_{1-4} alkylsulfonyl,
(xLiv) C_{6-10} arylsulfonyl,
(xLv) C_{1-4} alkoxy-carbonyloxy,
(xLvi) halo-C_{1-4} alkyl,
(xLvii) halo-C_{1-4} alkoxy, halo-C_{1-4} alkylthio, halo-C_{1-4} alkylsulfinyl or halo-C_{1-4} alkylsulfonyl,
(xLviii) cyano, nitro, hydroxyl, carboxyl, sulfo, phosphono,
(xLix) C_{1-4} alkyloxysulfonyl,
(L) C_{6-10} aryloxysulfonyl,
(Li) C_{7-12} aralkyloxysulfonyl, and
(Lii) di-C_{1-4} alkyloxyphosphoryl group, with the proviso that when R^2 is a hydrogen atom, R^1 is a group of the formula,



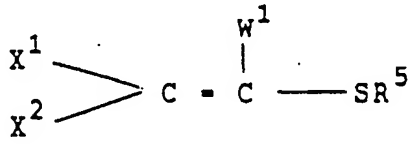
[wherein R^{3a} is hydrogen, C_{1-4} alkyl, C_{7-9} phenylalkyl or C_{1-4} alkanoyl and R^{4a} is a hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy-C_{1-4} alkyl, (di-C_{1-4} alkylamino)-C_{1-4} alkyl, tri-C_{1-4} alkylsilyl-C_{1-4} alkyl, C_{2-4} alkenyl or pyridyl- or thiazolyl-C_{1-2} alkyl wherein pyridyl or thiazolyl moiety may optionally be substituted with a halogen atom, or R^{3a} and R^{4a} taken together with the adjacent nitrogen atom constitute pyrrolidino] and A^o is pyridyl, pyrazinyl or thiazolyl, each of which may optionally be substituted with a halogen, C_{1-4} alkyl, C_{1-4} alkylthio or C_{1-4} alkoxy), and with the proviso that when



is O_2N-CH=;
R^1 is



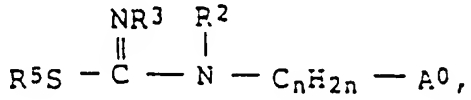
R^3 is hydrogen, C_{1-5} alkyl or C_{3-6} cycloalkyl;
R^4 is hydrogen, C_{1-5} alkyl, C_{3-6} cycloalkyl, benzyl or pyrimidinylmethyl; or
R^3 and R^4 together with the adjacent nitrogen atom constitute a cyclic amino group of pyrrolidinyl or piperazinyl; and
R^2 is hydrogen, C_{1-5} alkyl or C_{3-6} cycloalkyl,
A^0 is not a pyridyl subsituted by C_{1-4} haloalkyl, C_{1-4} haloalkoxy, C_{1-4} haloalkylthio, C_{1-4} haloalkylsulfinyl, C_{1-4} haloalkylsulfonyl, cyano, nitro or hydroxyl,
or a salt thereof,
which comprises
(1) reacting a compound of the formula:

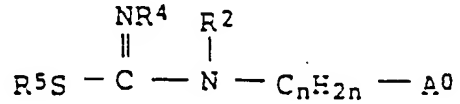


or a salt thereof with a compound of the formula:

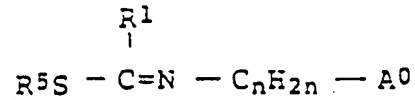
$Y - W^2$

or a salt thereof, or
(2) reacting a compound of the formula:

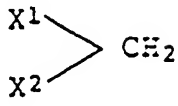




or

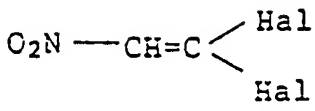


or a salt thereof with a compound of the formula:



or a salt thereof, or

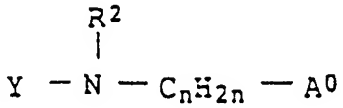
(3) reacting a compound of the formula:



or

O_2N - $CH_2C(Hal)_3$

(i) with a compound of the formula:



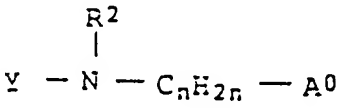
or a salt thereof, and then reacting the resulting product with a compound of the formula:

R^1 - Y

or a salt thereof, or (ii) with a compound of the formula:

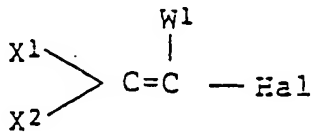
R^1 - Y

or a salt thereof, and then reacting the resulting product with a compound of the formula:



or a salt thereof, or

(4) reacting a compound of the formula:

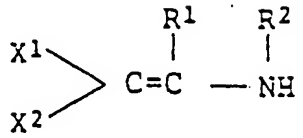


or a salt thereof with a compound of the formula:

Y - W^2

or a salt thereof, or

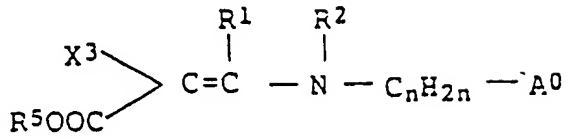
(5) reacting a compound of the formula:



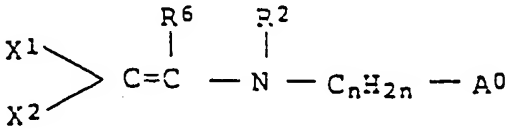
or a salt thereof with a compound of the formula:

$A^0 - C_nH_{2n} - Hal$

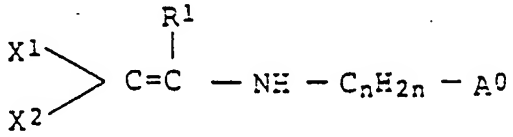
or a salt thereof, or
(6) subjecting a compound of the formula:



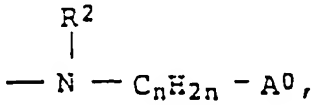
or a salt thereof to hydrolysis reaction and then to decarboxylation reaction, or
(7) subjecting a compound of the formula:



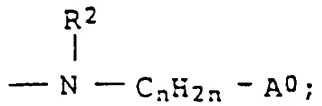
or



or a salt thereof to alkylation, acylation, alkoxycarbonylation, sulfonylation or phosphorylation, in which formulas, R^5 is a C_{1-4} alkyl or aralkyl; when W^1 is



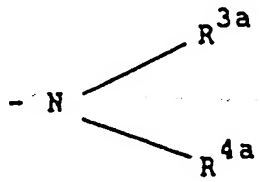
W^2 is R^1 and when W^1 is R^1, W^2 is



Y is a hydrogen atom or an alkali metal;
R^3 is a hydrogen atom, alkyl, aryl aralkyl, heterocyclic, acyl, alkoxycarbonyl, aryloxycarbonyl,

heterocycleoxycarbonyl, arylsulfonyl, alkylsulfonyl, dialkoxyphosphoryl, alkoxy, hydroxyl, amino, dialkylamino, acylamino, alkoxycarbonylamino, alkylsulfonylamino, dialkoxyphosphorylamino, aralkyloxy or alkoxycarbonylalkyl; R^4 is a hydrogen atom, or alkyl, cycloalkyl, alkenyl, cyoloalkenyl or alkynyl which groups may optionally be substituted, or pyridyl- or thiazolyl-C_{1-2} alkyl wherein pyridyl and thiazolyl moiety may optionally be substituted with a halogen atom; Hal is a halogen atom;
X^3 is an electron-attracting group; R^5 is a group attached through a nitrogen atom containing at least one hydrogen atom; and X^1, X^2, R^1, R^2, n and A^0 are defined as above.

2. A process as claimed in claim 1, wherein R^2 is hydrogen, R^1 is a group of the formula:



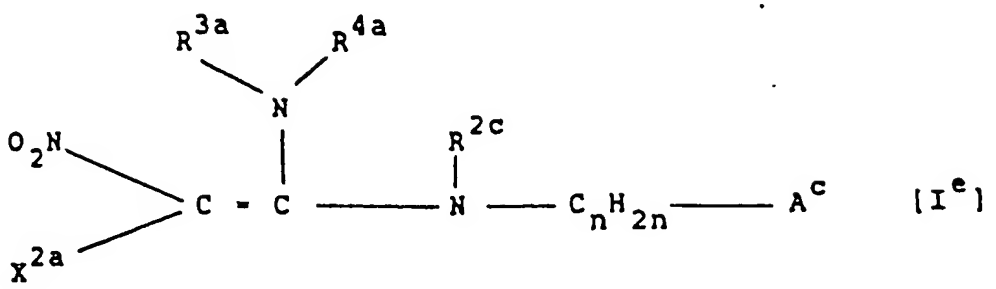
(wherein R^{3a} and R^{4a} are as defined in claim 1) and A^0 is heterocycle selected from the class consisting of pyridyl, pyrazinyl and thiazolyl, the said heterocycle mentioned just above for A^0 being optionally substituted with halogen, C_{1-4} alkyl, C_{1-4} alkylthio or C_{1-4} alkoxy.

3. A process as claimed in claim 1, wherein R^2 in other than hydrogen.

4. A process as claimed in claim 1, wherein:
X^1 is nitro;
X^2 is hydrogen, C_{1-2} alkoxycarbonyl or C_{1-2} alkylsulfonylthiocarbamoyl;
R^1 is amino, mono- or di-C_{1-4} alkylamino, halo-C_{1-4} alkylamino, N-C_{1-4} alkyl-N-C_{1-2} alkanoylamino, N-halo-C_{1-4} alkyl-N-C_{1-2} alkanoylamino or C_{1-2} alkanoylamino;
R^2 is hydrogen, C_{1-2} alkoxy, di-C_{1-2} alkylamino, C_{1-4} alkyl, halo-C_{1-4} alkyl or C_{1-2} alkanoyl;
n is 0 or 1;
A^0 is 2- or 3-thienyl, 2- or 3-furyl, 2- or 3-pyrrolyl, 2-, 3- or 4-pyridyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxido-2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxido-2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxido-3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]-pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl or phenoxyazinyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl, halo-C_{1-4} alkyl, C_{1-4} alkoxy, halo-C_{1-4} alkoxy, C_{1-4} alkylthio or halo-C_{1-4} alkylthio or a salt thereof.

5. A as claimed in claim 1, wherein:
X^1 is nitro;
X^2 is hydrogen or C_{1-2} alkylsulfonylthiocarbamoyl;
R^1 is amino, mono- or di-C_{1-2} alkylamino, halo-C_{1-2} alkylamino, N-C_{1-2} alkyl-N-C_{1-2} alkanoylamino, N-halo-C_{1-2} alkyl-N-C_{1-2} alkanoylamino or C_{1-2} alkanoylamino;
R^2 is hydrogen, C_{1-2} alkoxy, di-C_{1-2} alkylamino, C_{1-4} alkyl, halo-C_{1-4} alkyl or C_{1-2} alkanoyl;
n is 1; and
A^0 is pyridyl, pyrazinyl or thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl, halo-C_{1-4} alkyl, C_{1-4} alkoxy, halo-C_{1-4} alkoxy, C_{1-4} alkylthio or halo-C_{1-4} alkylthio or a salt thereof.

6. A process as claimed in claim 1 for preparing a compound of the formula



[I^e]

wherein:

X^{2a} is hydrogen, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl;

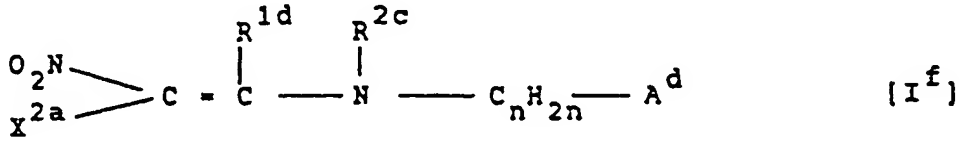
R^{2c} is hydrogen, C_{1-3} alkanoyl, C_{1-4} alkyl, mono- or- di-C_{1-4} alkoxy-C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di-C_{1-4} alkylamino or C_{1-4} alkoxy;

A^c is 3- or 4-pyridyl, pyrazinyl or 4- or 5-thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy;

n is 1; and

R^{3a} and R^{4a} are as defined in claim 1 , or a salt thereof.

7. A process as claimed in claim 1 for preparing a compound of the formula:



[I^f]

wherein:

X^{2a} is hydrogen, C_{1-4} alkoxycarbonyl or C_{1-4} alkylsulfonylthiocarbamoyl;

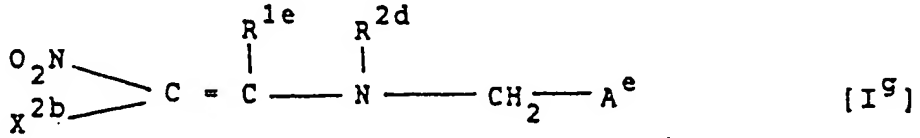
R^{1d} is amino, mono- or di-C_{1-4} alkylamino, N-C_{1-4} alkyl-N-C_{1-3} alkanoylamino C_{7-9} aralkylamino, halogenothiazolyl-C_{1-2} alkylamino or C_{1-4} alkoxy-C_{1-2} alkylamino;

R^{2c} is hydrogen, C_{1-3} alkanoyl, C_{1-4} alkyl, mono- or di-C_{1-4} alkoxy-C_{1-4} alkyl, C_{7-9} aralkyl, mono- or di-C_{1-4} alkylamino or C_{1-4} alkoxy;

n is 0, 1 or 2; and

A^d is 3- or 4-pyridyl, pyrazinyl or 5-thiazolyl, each of which may optionally be substituted with halogen, C_{1-4} alkyl or C_{1-4} alkoxy, or a salt thereof.

8. A process as claimed in claim 1 for preparing a compound of the formula:



[I^g]

wherein:

X^{2b} is hydrogen or C_{1-2} alkylsulfonylthiocarbamoyl;

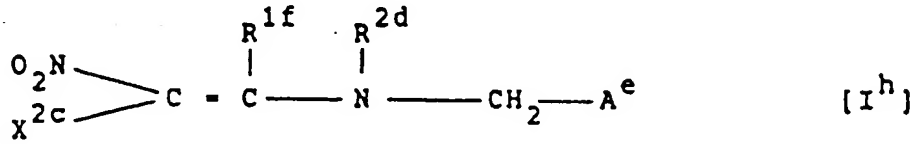
R^{1e} is amino, mono- or di-C_{1-2} alkylamino or N-C_{1-2} alkyl-N-formylamino;

R^{2d} is hydrogen, C_{1-2} alkyl or C_{1-3} alkanoyl; and

A^e is a group of the formula:

wherein Hal is a halogen atom , or a salt thereof.

9. A process as claimed in claim 1 for preparing a compound of the formula:

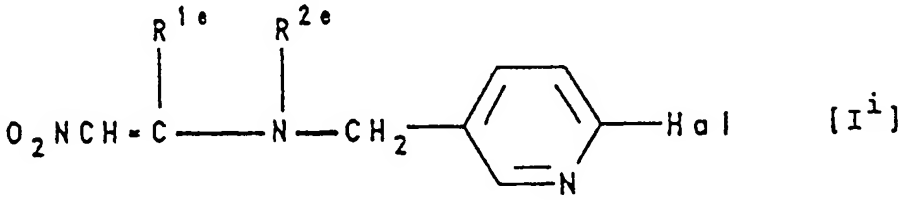


wherein:

X^{2c} is hydrogen or methylsulfonylthiocarbamoyl;
R^{1f} is amino, methylamino, dimethylamino or N-methyl-N-formylamino;
R^{2d} is a hydrogen atom, formyl or C_{1-2} alkyl; and
A^e is a group of the formula:

wherein Hal is a halogen atom, or a salt thereof.

10. A process as claimed in claim 1 for preparing a compound of the formula:



wherein:

R^{1e} is amino, mono- or di-C_{1-2} alkylamino or N-C_{1-2} alkyl-N-formylamino;
R^{2e} is C_{1-2} alkyl or formyl; and
Hal is a halogen atom , or a salt thereof.

11. A process as claimed in claim 1, wherein the heterocycle is selected from the following group and being optionally substituted as defined in claim 1, the group consisting of 2- or 3-thienyl, 2- or 3-furyl, 2- or 3- pyrrolyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxido-2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxido-2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxido-3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]pyridazinyl, oxoimidazinyl, dioxotriazinyl, pyrrolidinyl, piperidinyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinox-

alinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl and phenoxazinyl.

12. A process as claimed in claim 1 for the preparation of a compound selected from 1-[N-(6-chloro-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylene, 1-(6-chloro-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylene, and 1-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylene.

13. A process for preparing an insecticidal/miticidal composition which comprises mixing an insecticidal/miticidal effective amount of at least one of the α-unsaturated amines as prepared according to any one of claims 1 to 12, or a salt thereof, together with a suitable carrier or carriers.

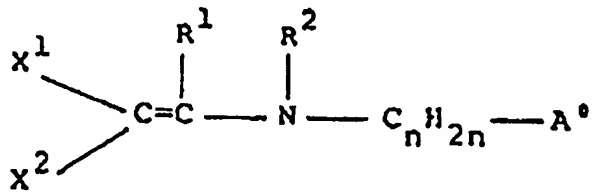
14. A method of combatting undesirable insects or mites, which comprises applying an insecticidal or miticidal effective amount of the compound of the formula [I°] prepared according to any one of claims 1 to 12 or a salt thereof to the said insects or mites or their habitat.

15. A method of claim 14, wherein the compound or salt is applied in a composition of the compound or salt with a suitable carrier or carriers.

Patentansprüche

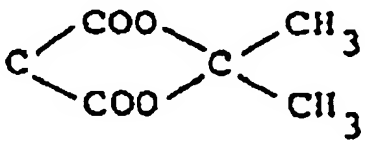
Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. α-Ungesättigtes Amin der Formel

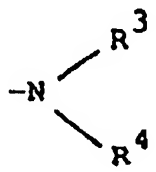


[I°]

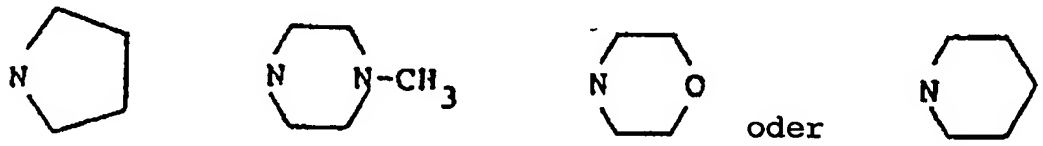
worin
eines von X^1 und X^2 eine elektronenanziehende Gruppe ist und das andere ein Wasserstoffatom oder eine elektronenanziehende Gruppe ist, in welcher die elektronenanziehende Gruppe Cyano, Nitro, C_{1-4}-Alkoxycarbonyl, Carboxy, C_{6-10}-Aryloxycarbonyl, Heterocyclyloxycarbonyl, C_{1-4}-Alkylsulfonyl, welches mit Halogen substituiert sein kann, Aminosulfonyl, Di-C_{1-4}-alkoxyphosphoryl, C_{1-4}-Alkanoyl, welches mit Halogen substituiert sein kann, C_{1-4}-Alkylsulfonylthiocarbamoyl, Carbamoyl oder Halogen ist, oder X^1 und X^2 zusammen mit dem Kohlenstoffatom, an welches sie gebunden sind, einen Ring der Formel



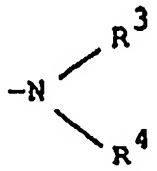
bilden;
R^1 eine Gruppe der Formel



ist, in welcher
R^3 Wasserstoff, C_{1-20}-Alkyl, C_{6-10}-Aryl, C_{7-9}-Aralkyl, Heterocyclyl, C_{1-4}-Alkanoyl, C_{6-10}-Arylcarbonyl, C_{1-4}-Alkoxycarbonyl, C_{6-10}-Aryloxycarbonyl, Heterocyclyloxycarbonyl, C_{6-10}-Arylsulfonyl, C_{1-4}-Alkylsulfonyl, Di-C_{1-4}-alkoxyphosphoryl, C_{1-4}-Alkoxy, Hydroxy, Amino, Di-C_{1-4}-alkylamino, C_{1-4}-Alkanoylamino, C_{1-4}-Alkoxycarbonylamino, C_{1-4}-Alkylsulfonylamino, Di-C_{1-4}-alkoxyphosphorylamino, C_{7-9}-Aralkyloxy oder C_{1-4}-Alkoxycarbonyl-C_{1-4}-alkyl ist, und
R^4 Wasserstoff, C_{1-20}-Alkyl, C_{3-6}-Cycloalkyl, C_{2-6}-Alkenyl, C_{3-6}-Cycloalkenyl oder C_{2-6}-Alkinyl ist, wobei jedes der für R^4 definierten Reste außer Wasserstoff gegebenenfalls durch 1 bis 3 Substituenten substituiert sein kann, welche aus der aus Hydroxy, C_{1-4}-Alkoxy, Halogen, Di-C_{1-4}-alkylamino, C_{1-4}-Alkylthio, C_{1-3}-Alkanoylamino, C_{1-4}-Alkylsulfonylamino, Tri-C_{1-4}-alkylsilyl, Pyridyl und Thiazolyl bestehenden Gruppe ausgewählt sind, und jedes Pyridyl und Thiazolyl durch Halogen weiter substituiert sein kann, oder
R^3 und R^4 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe der Formel



bilden,
R^2 (1) Wasserstoff, (2) eine über ein Kohlenstoffatom gebundene Gruppe, welche aus der Klasse ausgewählt ist, die aus C_{1-4}-Alkanoyl, C_{1-20}-Alkyl, C_{2-6}-Alkenyl, C_{3-6}-Cycloalkyl, C_{6-10}-Aryl, C_{7-9}-Aralkyl und 3- oder 4-Pyridyl besteht, wobei die über ein Kohlenstoff gebundene Gruppe gegebenenfalls durch 1 bis 3 Substituenten substituiert ist, welche aus der Klasse ausgewählt sind, die aus C_{1-4}-Alkylthio, C_{1-4}-Alkoxy, Mono- oder Di-C_{1-4}-alkylamino, C_{1-4}-Alkoxycarbonyl, C_{1-4}-Alkylsulfonyl, Halogen und C_{1-4}-Alkanoyl besteht, (3) eine über ein Sauerstoffatom gebundene Gruppe, welche aus der Klasse ausgewählt ist, die aus C_{1-4}-Alkoxy, C_{3-6}-Cycloalkoxy, C_{2-4}-Alkenyloxy, C_{3-6}-Cycloalkenyloxy, Ethinyloxy, C_{6-10}-Aryloxy, Thienyloxy und Hydroxy besteht, wobei die über ein Sauerstoffatom gebundene Gruppe gegebenenfalls durch 1 bis 3 Substituenten substituiert ist, welche aus der Klasse ausgewählt sind, die aus Halogen und Phenyl besteht, oder (4) eine über ein Stickstoffatom gebundene Gruppe der Formel

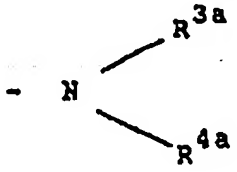


ist, worin
R^3 und R^4 die vorstehend angegebenen Bedeutungen besitzen,
n eine ganze Zahl 0, 1 oder 2 ist,
A° ein Heterocyclus ist,
wobei der Heterocyclus in dem Heterocyclylcarbonyl für X^1 und X^2, der Heterocyclus für R^3, der Heterocyclus in dem Heterocyclyloxycarbonyl für R^3 und der Heterocyclus für A° ein aus der Klasse ausgewähltes Mitglied ist, welche aus Thienyl, Furyl, Pyrrolyl, Pyridyl, Oxazolyl, Thiazolyl, Pyrazolyl, Imidazolyl, Isoxazolyl, Isothiazolyl, Oxadiazolyl, Thiadiazolyl, Triazolyl, Tetrazolyl, N-Oxidopyridyl, Pyrimidinyl, N-Oxidopyrimidinyl, Pyridazinyl, Pyrazinyl, N-Oxidopyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxatriazinyl, Tetrazo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl besteht, wobei der Heterocyclus gegebenenfalls durch 1 bis 5 Substituenten substituiert ist, welche aus der Gruppe ausgewählt sind, die aus
(i) C_{1-4}-Alkyl

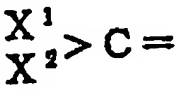
(ii) C_{3-6}-Cycloalkyl
(iii) C_{6-10}-Aryl
(iv) C_{1-4}-Alkoxy
(v) C_{3-6}-Cycloalkyloxy
(vi) C_{6-10}-Aryloxy
(vii) C_{7-12}-Aralkyloxy
(viii) C_{1-4}-Alkylthio
(ix) C_{3-6}-Cycloalkylthio
(x) C_{6-10}-Arylthio
(xi) C_{7-12}-Aralkylthio
(xii) Mono-C_{1-4}-alkylamino
(xiii) Di-C_{1-4}-alkylamino
(xiv) C_{3-6}-Cycloalkylamino
(xv) C_{6-10}-Arylamino
(xvi) C_{7-12}-Aralkylamino
(xvii) Halogen
(xviii) C_{1-4}-Alkoxycarbonyl
(xix) C_{6-10}-Aryloxycarbonyl
(xx) C_{3-6}-Cycloalkyloxycarbonyl
(xxi) C_{7-12}-Aralkyloxycarbonyl
(xxii) C_{1-5}-Alkanoyl
(xxiii) C_{1-15}-Alkanoyloxy
(xxiv) Carbamoyl, N-Methylcarbamoyl, N,N-Dimethylcarbamoyl, N-Ethylcarbamoyl, N,N-Diethylcarbamoyl, N-Phenylcarbamoyl, Pyrrolidinocarbamoyl, Piperidinocarbamoyl, Piperazinocarbamoyl, Morpholinocarbamoyl oder N-Benzylcarbamoyl,
(xxv) N-Methylcarbamoyloxy, N,N-Dimethylcarbamoyloxy, N-Ethylcarbamoyloxy, N-Benzylcarbamoyloxy, N,N-Dibenzylcarbamoyloxy oder N-Phenylcarbamoyloxy,
(xxvi) C_{1-4}-Alkanoylamino,
(xxvii) C_{6-10}-Arylcarbonylamino,
(xxviii) C_{1-4}-Alkoxycarbonylamino,
(xxix) C_{7-12}-Aralkyloxycarbonyl,
(xxx) Methansulfonylamino, Ethansulfonylamino, Butansulfonylamino, Benzolsulfonylamino, Toluolsulfonylamino, Naphthalinsulfonylamino, Trifluormethansulfonylamino, 2-Chlorethansulfonylamino oder 2,2,2-Trifluormethansulfonylamino,
(xxxi) Pyrrolidinyl, Pyrrolyl, Pyrazolyl, Imidazolyl, Furyl, Thienyl, Oxazolyl, Isoxazolyl, Isothiazolyl, Thiazolyl, Piperidinyl, Pyridyl, Piperazinyl, Pyrimidinyl, Pyranyl, Tetrahydropyranyl, Tetrahydrofuryl, Indolyl, Chinolyl, 1,3,4-Oxadiazolyl, Thieno[2,3-d]pyridyl, 1,2,3-Thiadiazolyl, 1,3,4-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1,3,4-Triazolyl, Tetrazolyl, 4,5-Dihydro-1,3-dioxazolyl, Tetrazolo[1,5-b]-pyridazinyl, Benzothiazolyl, Benzoxazolyl, Benzimidazolyl oder Benzothienyl,
(xxxii) einer Heterocyclylthio-, Heterocyclyloxy-, Heterocyclylamino- oder Heterocyclylcarbonylaminogruppe, welche aus dem Binden irgendeiner der vorstehend definierten heterocyclischen Gruppen (xxxi) an das S-, O-, N-Atom oder eine Carbonylaminogruppe stammt,
(xxxiii) Di-C_{1-4}-alkylphosphinothioylamino,
(xxxiv) Methoxyimino, Ethoxyimino, 2-Fluorethoxyimino, Carboxymethoxyimino, 1-Carboxy-1-methylethoxyimino, 2,2,2-Trichlorethoxycarbonylmethoxyimino, 1-(2,2,2-Trichlorethoxycarbonyl)-1-methylethoxyimino, (2-Aminothiazol-4-yl)methoxyimino oder (1H-Imidazol-4-yl)methoxyimino,
(xxxv) C_{1-4}-Alkylsulfonyloxy,
(xxxvi) C_{6-10}-Arylsulfonyloxy,
(xxxvii) Di-C_{6-10}-arylphosphinothioylamino,
(xxxviii) Thiocarbamoylthio, N-Methylthiocarbamoylthio, N,N-Dimethylthiocarbamoylthio, N-Ethylthiocarbamoylthio, N-Benzylthiocarbamoylthio, N,N-Dibenzylthiocarbamoylthio oder N-Phenylthiocarbamoylthio,
(xxxix) Trimethylsilyloxy, t-Butyldimethylsilyloxy, t-Butyldiphenylsilyloxy oder Dimethylphenylsilyloxy,
(xL) Trimethylsilyl, t-Butyldimethylsilyl, t-Butyldiphenylsilyl oder Dimethylphenylsilyl,
(xLi) C_{1-4}-Alkylsulfinyl,
(xLii) C_{6-10}-Arylsulfinyl,
(xLiii) C_{1-4}-Alkylsulfonyl,
(xLiv) C_{6-10}-Arylsulfonyl,

(xLv) C_{1-4}-Alkoxycarbonyloxy,
(xLvi) Halogen-C_{1-4}-alkyl,
(xLvii) Halogen-C_{1-4}-alkoxy, Halogen-C_{1-4}-alkylthio, Halogen-C_{1-4}-alkylsulfinyl oder Halogen-C_{1-4}-alkylsulfonyl,
(xLviii) Cyano, Nitro, Hydroxyl, Carboxyl, Sulfo, Phosphono,
(xLix) C_{1-4}-Alkyloxysulfonyl,
(L) C_{6-10}-Aryloxysulfonyl,
(Li) C_{7-12}-Aralkyloxysulfonyl und
(Lii) einer Di-C_{1-4}-alkyloxyphosphorylgruppe besteht,

mit der Maßgabe, daß wenn R^2 ein Wasserstoffatom ist, R^1 eine Gruppe der Formel



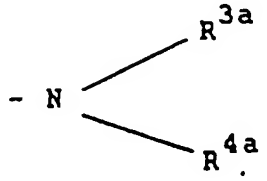
ist [worin R^{3a} Wasserstoff, C_{1-4}-Alkyl, C_{7-9}-Phenylalkyl oder C_{1-4}-Alkanoyl ist und R^{4a} Wasserstoff, C_{1-4}-Alkyl, C_{1-4}-Alkoxy-C_{1-4}-alkyl, (Di-C_{1-4}-alkylamino)-C_{1-4}-alkyl, Tri-C_{1-4}-alkylsilyl-C_{1-4}-alkyl, C_{2-4}-Alkenyl oder Pyridyl- oder Thiazolyl-C_{1-2}-alkyl ist, worin der Pyridyl- oder Thiazolylteil gegebenenfalls mit einem Halogenatom substituiert sein kann, oder R^{3a} und R^{4a} mit dem benachbarten Stickstoffatom zusammengenommen Pyrrolidino bilden] und A° Pyridyl, Pyrazinyl oder Thiazolyl ist, wovon jedes gegebenenfalls mit einem Halogen, C_{1-4}-Alkyl, C_{1-4}-Alkylthio oder C_{1-4}-Alkoxy substituiert sein kann,
und mit der Maßgabe, daß wenn



O_2N-CH= ist,
R^1

ist,
R^3 Wasserstoff, C_{1-5}-Alkyl oder C_{3-6}-Cycloalkyl ist,
R^4 Wasserstoff, C_{1-5}-Alkyl, C_{3-6}-Cycloalkyl, Benzyl oder Pyrimidinylmethyl ist, oder
R^3 und R^4 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe Pyrrolidinyl oder Piperazinyl bilden und
R^2 Wasserstoff, C_{1-5}-Alkyl oder C_{3-6}-Cycloalkyl ist,
A° kein durch C_{1-4}-Halogenalkyl, C_{1-4}-Halogenalkoxy, C_{1-4}-Halogenalkylthio, C_{1-4}-Halogenalkylsulfinyl, C_{1-4}-Halogenalkylsulfonyl, Cyano, Nitro oder Hydroxyl substituiertes Pyridyl ist,
oder ein Salz derselben.

2. Verbindung wie in Anspruch 1 beansprucht, worin R^2 Wasserstoff ist, R^1 eine Gruppe der Formel



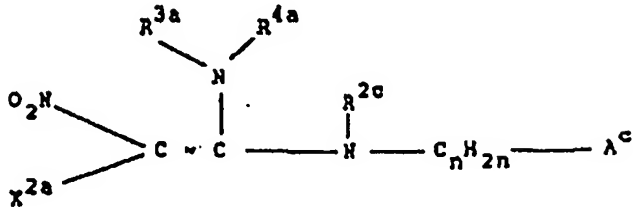
ist (worin R^{3a} und R^{4a} wie in Anspruch 1 definiert sind) und A° ein aus der Klasse ausgewählter Heterocyclus ist, welche aus Pyridyl, Pyrazinyl und Thiazolyl besteht, wobei der unmittelbar voranstehend für A° angeführte Keterocyclus gegebenenfalls mit Halogen, C_{1-4}-Alkyl, C_{1-4}-Alkylthio oder C_{1-4}-Alkoxy substituiert ist.

3. Verbindung wie in Anspruch 1 beansprucht, worin R^2 von Wasserstoff verschieden ist.

4. Verbindung wie in Anspruch 1 beansprucht, worin
X^1 Nitro ist,
X^2 Wasserstoff, C_{1-2}-Alkoxycarbonyl oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^1 Amino, Mono- oder Di-C_{1-4}-alkylamino, Halogen-C_{1-4}-alkylamino, N-C_{1-4}-Alkyl-N-C_{1-2}-alkanoylamino, N-Halogen-C_{1-4}-alkyl-N-C_{1-2}-alkanoylamino oder C_{1-2}-Alkanoylamino ist,
R^2 Wasserstoff, C_{1-2}-Alkoxy, Di-C_{1-2}-alkylamino, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl oder C_{1-2}-Alkanoyl ist,
n 0 oder 1 ist,
A° 2- oder 3-Thienyl, 2- oder 3-Furyl, 2- oder 3-Pyrrolyl, 2-, 3- oder 4-Pyridyl, 2-, 4- oder 5-Oxazolyl, 2-, 4- oder 5-Thiazolyl, 3-, 4- oder 5-Pyrazolyl, 2-, 4- oder 5-Imidazolyl, 3-, 4-oder 5-Isoxazolyl, 3-, 4- oder 5-Isothiazolyl, 3- oder 5-(1,2,4-Oxadiazolyl), 1,3,4-Oxadiazolyl, 3- oder 5-(1,2,4-Thiadiazolyl), 1,3,4-Thiadiazolyl, 4- oder 5-(1,2,3-Thiadiazolyl), 1,2,5-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1H- oder 2H-Tetrazolyl, N-Oxido-2-, 3- oder 4-pyridyl, 2-, 4- oder 5-Pyrimidinyl, N-Oxido-2-, 4- oder 5-pyrimidinyl, 3- oder 4-Pyridazinyl, Pyrazinyl, N-Oxido-3- oder 4-pyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl oder Phenoxazinyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl, C_{1-4}-Alkoxy, Halogen-C_{1-4}-alkoxy, C_{1-4}-Alkylthio oder Halogen-C_{1-4}-alkylthio substituiert sein kann, oder ein Salz derselben.

5. Verbindung wie in Anspruch 1 beansprucht, worin
X^1 Nitro ist,
X^2 Wasserstoff oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^1 Amino, Mono- oder Di-C_{1-2}-alkylamino, Halogen-C_{1-2}-alkylamino, N-C_{1-2}-Alkyl-N-C_{1-2}-alkanoylamino, N-Halogen-C_{1-2}-alkyl-N-C_{1-2}-alkanoylamino oder C_{1-2}-Alkanoylamino ist,
R^2 Wasserstoff, C_{1-2}-Alkoxy, Di-C_{1-2}-alkylamino, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl oder C_{1-2}-Alkanoyl ist,
n 1 ist, und
A° Pyridyl, Pyrazinyl oder Thiazolyl ist, wovon jedes gegebenenfalls mit Kalogen, C_{1-4}-Alkyl , Halogen-C_{1-4}-alkyl, C_{1-4}-Alkoxy, Halogen-C_{1-4}-alkoxy, C_{1-4}-Alkylthio oder Halogen-C_{1-4}-alkylthio substituiert sein kann, oder ein Salz derselben.

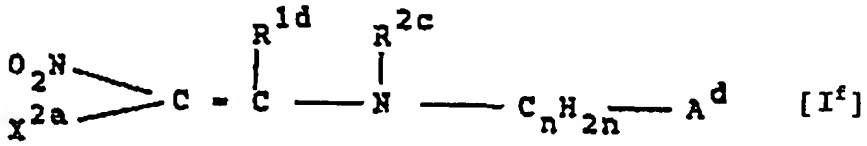
6. Verbindung wie in Anspruch 1 beansprucht mit der Formel



[I^e]

worin
X^{2a} Wasserstoff, C_{1-4}-Alkoxycarbonyl oder C_{1-4}-Alkylsulfonylthiocarbamoyl ist,
R^{2c} Wasserstoff, C_{1-3}-Alkanoyl, C_{1-4}-Alkyl, Mono- oder Di-C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{7-9}-Alalkyl, Mono- oder Di-C_{1-4}-alkylamino oder C_{1-4}-Alkoxy ist,
A^c 3- oder 4-Pyridyl, Pyrazinyl oder 4- oder 5-Thiazolyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl oder C_{1-4}-Alkoxy substituiert sein kann,
n 1 ist und
R^{3a} und R^{4a} wie in Anspruch 1 definiert sind, oder ein Salz derselben.

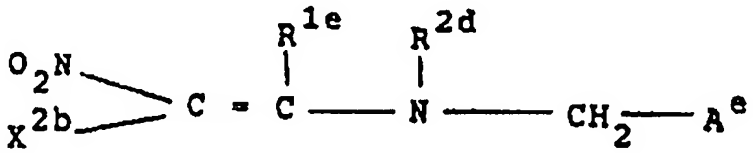
7. Verbindung wie in Anspruch 1 beansprucht, welche eine Verbindung der Formel



[I^f]

ist, worin
X^{2a} Wasserstoff, C_{1-4}-Alkoxycarbonyl oder C_{1-4}-Alkylsulfonylthiocarbamoyl ist,
R^{1d} Amino, Mono- oder Di-C_{1-4}-alkylamino, N-C_{1-4}-Alkyl-N-C_{1-3}-alkanoylamino, C_{7-9}-Aralkylamino, Halogenthiazolyl-C_{1-2}-alkylamino oder C_{1-4}-Alkoxy-C_{1-2}-alkylamino ist,
R^{2c} Wasserstoff, C_{1-3}-Alkanoyl, C_{1-4}-Alkyl, Mono- oder Di-C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{7-9}-Aralkyl, Mono- oder Di-C_{1-4}-alkylamino oder C_{1-4}-Alkoxy ist,
n 0, 1 oder 2 ist und
A^d 3- oder 4-Pyridyl, Pyrazinyl oder 5-Thiazolyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl oder C_{1-4}-Alkoxy substituiert sein kann, oder ein Salz derselben.

8. Verbindung wie in Anspruch 1 beansprucht, welche eine Verbindung der Formel

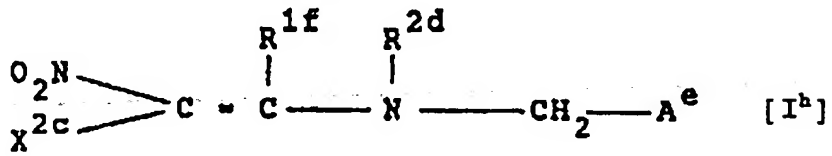


[I^g]

ist, worin
X^{2b} Wasserstoff oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^{1e} Amino, Mono- oder Di-C_{1-2}-alkylamino oder N-C_{1-2}-Alkyl-N-formylamino,
R^{2d} Wasserstoff, C_{1-2}-Alkyl oder C_{1-3}-Alkanoyl ist und
A^e eine Gruppe der Formel

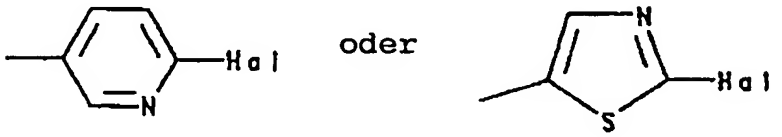
ist, worin Hal ein Halogenatom ist, oder ein Salz derselben.

9. Verbindung wie in Anspruch 1 beansprucht, welche eine Verbindung der Formel



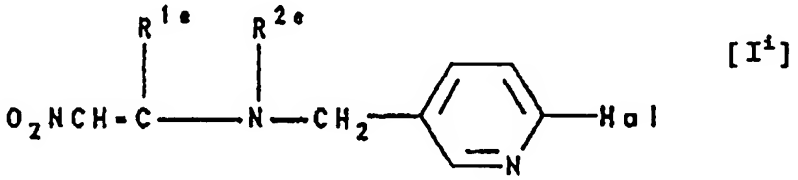
[I^h]

ist, worin
X^{2c} Wasserstoff oder Methylsulfonylthiocarbamoyl ist,
R^{1f} Amino, Methylamino, Dimethylamino oder N-Methyl-N-formylamino ist,
R^{2d} ein Wasserstoffatom, Formyl oder C_{1-2}-Alkyl ist und
A^e eine Gruppe der Formel



ist, worin Hal ein Halogenatom ist, oder ein Salz derselben.

10. Verbindung wie in Anspruch 1 beansprucht, welche eine Verbindung der Formel



[I^i]

ist, worin
R^{1e} Amino, Mono- oder Di-C_{1-2}-alkylamino oder N-C_{1-2}-Alkyl-N-formylamino ist,
R^{2e} C_{1-2}-Alkyl oder Formyl ist und
Hal ein Halogenatom ist, oder ein Salz derselben.

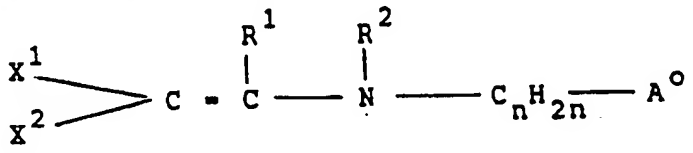
11. Verbindung wie in Anspruch 1 beansprucht, worin der Heterocyclus aus der folgenden Gruppe ausgewählt ist und gegebenenfalls wie in Anspruch 1 definiert substituiert ist, wobei die Gruppe aus 2- oder 3-Thienyl, 2- oder 3-Furyl, 2- oder 3-Pyrrolyl, 2-, 4- oder 5-Oxazolyl, 2-, 4- oder 5-Thiazolyl, 3-, 4- oder 5-Pyrazolyl, 2-, 4- oder 5-Imidazolyl, 3-, 4- oder 5-Isoxazolyl, 3-, 4- oder 5-Isothiazolyl, 3- oder 5-(1,2,4-Oxadiazolyl), 1,3,4-Oxadiazolyl, 3- oder 5-(1,2,4-Thiadiazolyl), 1,3,4-Thiadiazolyl, 4- oder 5-(1,2,3-Thiadiazolyl), 1,2,5-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1H- oder 2H-Tetrazolyl, N-Oxido-2-, 3- oder 4-pyridyl, 2-, 4- oder 5-Pyrimidinyl, N-Oxido-2-, 4- oder 5-pyrimidinyl, 3- oder 4-Pyridazinyl, Pyrazinyl, N-Oxido-3- oder 4-pyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl,

Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl besteht.

12. Verbindung wie in Anspruch 1 beansprucht, welche aus 1-[N-(6-Chlor-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylen, 1-(6-Chlor-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylen und 1-[N-(6-Chlor-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylen ausgewählt ist.

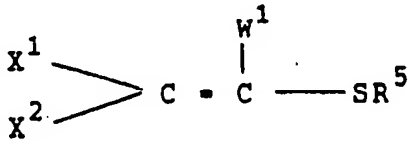
13. Insektizide/milbizide Zusammensetzung, welche eine insektizid/milbizid wirksame Menge wenigstens eines der in einem der Ansprüche 1 bis 12 beanspruchten α-ungesättigten Amine oder ein Salz derselben zusammen mit einem geeigneten Träger oder Trägern umfaßt.

14. Verfahren zu Herstellung eines α-ungesättigten Amins der Formel



[I°]

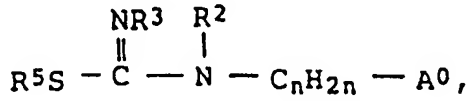
worin die Symbole wie in Anspruch 1 definiert sind oder eines Salzes derselben, welches das
(1) Umsetzen einer Verbindung der Formel

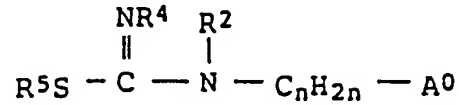


oder eines Salzes derselben mit einer Verbindung der Formel

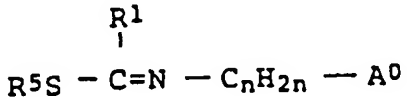
$Y - W^2$

oder einem Salz derselben, oder
(2) Umsetzen einer Verbindung der Formel

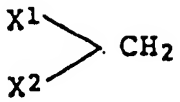




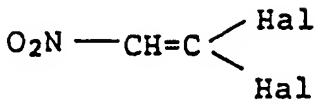
oder



oder eines Salzes derselben mit einer Verbindung der Formel



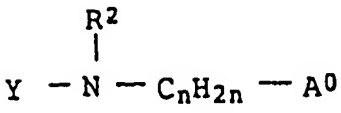
oder einem Salz derselben, oder
(3) Umsetzen einer Verbindung der Formel



oder

$O_2N - CH_2C(Hal)_3$

(i) mit einer Verbindung der Formel



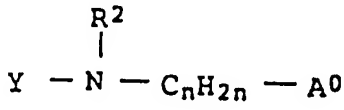
oder einem Salz derselben und anschließend das Umsetzen des sich daraus ergebenden Produkts mit einer Verbindung der Formel

$R^1 - Y$

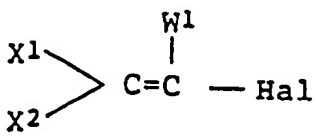
oder einem Salz derselben, oder (ii) mit einer Verbindung der Formel

$R^1 - Y$

oder einem Salz derselben und anschließend das Umsetzen des sich daraus ergebenden Produkts mit einer Verbindung der Formel



oder einem Salz derselben, oder
(4) Umsetzen einer Verbindung der Formel

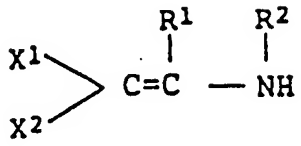


oder eines Salzes derselben mit einer Verbindung der Formel

$Y - W^2$

oder einem Salz derselben, oder

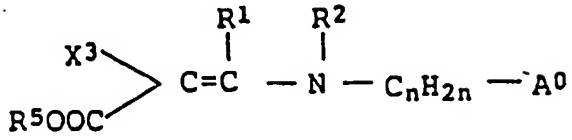
(5) Umsetzen einer Verbindung der Formel



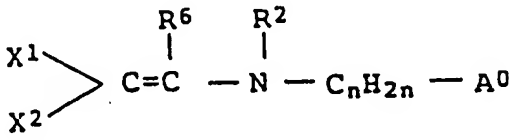
oder eines Salzes derselben mit einer Verbindung der Formel

$A^{\circ} - C_nH_{2n} - Hal$

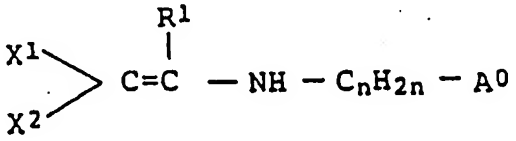
oder einem Salz derselben, oder
(6) Unterziehen einer Verbindung der Formel



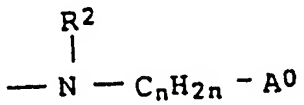
oder eines Salzes derselben einer Hydrolysereaktion und anschließend einer Decarboxylierungsreaktion, oder
(7) Unterziehen einer Verbindung der Formel



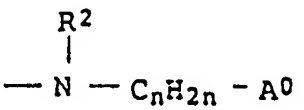
oder



oder eines Salzes derselben der Alkylierung, Acylierung, Alkoxycarbonylierung, Sulfonylierung oder Phosphorylierung, in welchen Formeln R^5 C_{1-4}-Alkyl oder Aralkyl ist; wenn W^1



ist, W^2 R^1 ist und wenn W^1 R^1 ist, W^2



ist; Y ein Wasserstoffatom oder ein Alkalimetall ist; R^3 ein Wasserstoffatom, Alkyl, Aryl, Aralkyl, Heterocyclyl, Acyl, Alkoxycarbonyl, Aryloxycarbonyl, Heterocyclyloxycarbonyl, Arylsulfonyl, Alkylsul-

fonyl, Dialkoxyphosphoryl, Alkoxy, Hydroxyl, Amino, Dialkylamino, Acylamino, Alkoxycarbonylamino, Alkylsulfonylamino, Dialkoxyphosphorylamino, Aralkyloxy oder Alkoxycarbonylalkyl ist; R^4 ein Wasserstoffatom oder Alkyl, Cycloalkyl, Alkenyl, Cycloalkenyl oder Alkinyl, welche Gruppen gegebenenfalls substituiert sein können, oder Pyridyl- oder Thiazolyl-C_{1-2}-alkyl ist, worin der Pyridyl- und Thiazolylteil gegebenenfalls mit einem Halogenatom substituiert sein kann; Hal ein Halogenatom ist; X^3 eine elektronenanziehende Gruppe ist; R^6 eine über ein Stickstoffatom gebundene Gruppe ist, welche wenigstens ein Wasserstoffatom enthält und X^1, X^2, R^1, R^2, n und A• wie in Anspruch 1 definiert sind.

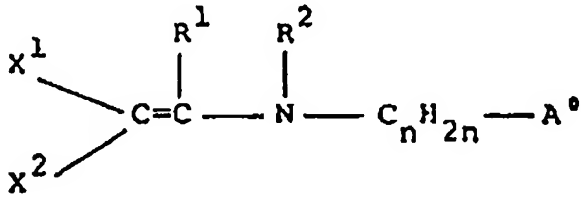
15. Verfahren zum Bekämpfen unerwünschter Insekten oder Milben, welches das Aufbringen einer insektizid oder milbizid wirksamen Menge der in einem der Ansprüche 1 bis 12 definierten Verbindung der Formel [I•] oder eines Salzes derselben auf die Insekten oder Milben oder ihren Lebensraum umfaßt.

16. Verfahren des Anspruchs 15, bei welchem die Verbindung oder das Salz in einer Zusammensetzung der Verbindung oder des Salzes mit einem geeigneten Träger oder Trägern angewandt wird.

17. Verfahren zum Bekämpfen unerwünschter Insekten oder Milben, welches das Aufbringen einer insektizid oder milbizid wirksamen Mengeder in Anspruch 12 definierten Verbindung der Formel [I•] umfaßt.

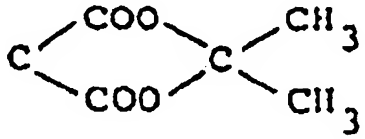
Patentansprüche für folgenden Vertragsstaat: ES

1. Verfahren zum Herstellen eines α-ungesättigten Amins der Formel

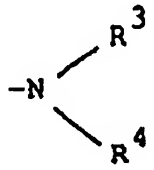


[I°]

worin
eines von X^1 und X^2 eine elektronenanziehende Gruppe ist und das andere ein Wasserstoffatom oder eine elektronenanziehende Gruppe ist, in welcher die elektronenanziehende Gruppe Cyano, Nitro, C_{1-4}-Alkoxycarbonyl, Carboxy, C_{6-10}-Aryloxycarbonyl, Heterocyclyloxycarbonyl, C_{1-4}-Alkylsulfonyl, welches mit Halogen substituiert sein kann, Aminosulfonyl, Di-$_{1-4}$-alkoxyphosphoryl, C_{1-4}-Alkanoyl, welches mit Halogen substituiert sein kann, C_{1-4}-Alkylsulfonylthiocarbamoyl, Carbamoyl oder Halogen ist, oder X^1 und X^2 zusammen mit dem Kohlenstoffatom, an welches sie gebunden sind, einen Ring der Formel



bilden;
R^1 eine Gruppe der Formel

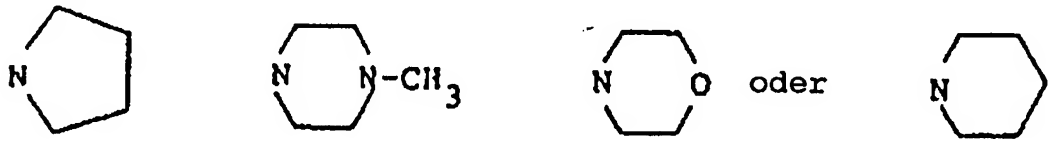


ist, in welcher

R^3 Wasserstoff, C_{1-20}-Alkyl, C_{6-10}-Aryl, C_{7-9}-Aralkyl, Heterocyclyl, C_{1-4}-Alkanoyl, C_{6-10}-Arylcarbonyl, C_{1-4}-Alkoxycarbonyl, C_{6-10}-Aryloxycarbonyl, Heterocyclyloxycarbonyl, C_{6-10}-Arylsulfonyl, C_{1-4}-Alkylsulfonyl, Di-C_{1-4}-alkoxyphosphoryl, C_{1-4}-Alkoxy, Hydroxy, Amino, Di-C_{1-4}-alkylamino, C_{1-4}-Alkanoylamino, C_{1-4}-Alkoxycarbonylamino, C_{1-4}-Alkylsulfonylamino, Di-C_{1-4}-alkoxyphosphorylamino, C_{7-9}-Aralkyloxy oder C_{1-4}-Alkoxycarbonyl-C_{1-4}-alkyl ist, und

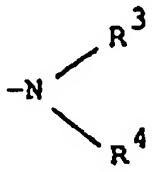
R^4 Wasserstoff, C_{1-20}-Alkyl, C_{3-6}-Cycloalkyl, C_{2-6}-Alkenyl, C_{3-6}-Cycloalkenyl oder C_{2-6}-Alkinyl ist, wobei jedes der für R^4 definierten Reste außer Wasserstoff gegebenenfalls durch 1 bis 3 Substituenten substituiert sein kann, welche aus der aus Hydroxy, C_{1-4}-Alkoxy, Halogen, Di-C_{1-4}-alkylamino, C_{1-4}-Alkylthio, C_{1-3}-Alkanoylamino, C_{1-4}-Alkylsulfonylamino, Tri-C_{1-4}-alkylsilyl, Pyridyl und Thiazolyl bestehenden Gruppe ausgewählt sind, und jedes Pyridyl und Thiazolyl durch Halogen weiter substituiert sein kann, oder

R^3 und R^4 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe der Formel



bilden,

R^2 (1) Wasserstoff, (2) eine über ein Kohlenstoffatom gebundene Gruppe, welche aus der Klasse ausgewählt ist, die aus C_{1-4}-Alkanoyl, C_{1-20}-Alkyl, C_{2-6}-Alkenyl, C_{3-6}-Cycloalkyl, C_{6-10}-Aryl, C_{7-9}-Aralkyl und 3- oder 4-Pyridyl besteht, wobei die über ein Kohlenstoff gebundene Gruppe gegebenenfalls durch 1 bis 3 Substituenten substituiert ist, welche aus der Klasse ausgewählt sind, die aus C_{1-4}-Alkylthio, C_{1-4}-Alkoxy, Mono- oder Di-C_{1-4}-alkylamino, C_{1-4}-Alkoxycarbonyl, C_{1-4}-Alkylsulfonyl, Halogen und C_{1-4}-Alkanoyl besteht, (3) eine über ein Sauerstoffatom gebundene Gruppe, welche aus der Klasse ausgewählt ist, die aus C_{1-4}-Alkoxy, C_{3-6}-Cycloalkoxy, C_{2-4}-Alkenyloxy, C_{3-6}-Cycloalkenyloxy, Ethinyloxy, C_{6-10}-Aryloxy, Thienyloxy und Hydroxy besteht ist, wobei die über ein Sauerstoffatom gebundene Gruppe gegebenenfalls durch 1 bis 3 Substituenten substituiert ist, welche aus der Klasse ausgewählt sind, die aus Halogen und Phenyl besteht, oder (4) eine über ein Stickstoffatom gebundene Gruppe der Formel



ist, worin

R^3 und R^4 die vorstehend angegebenen Bedeutungen besitzen,

n eine ganze Zahl 0, 1 oder 2 ist,

A° ein Heterocyclus ist,

wobei der Heterocyclus in dem Heterocyclylcarbonyl für X^1 und X^2, der Heterocyclus für R^3, der Heterocyclus in dem Heterocyclyloxycarbonyl für R^3 und der Heterocyclus für A° ein aus der Klasse ausgewähltes Mitglied ist, welche aus Thienyl, Furyl, Pyrrolyl, Pyridyl, Oxazolyl, Thiazolyl, Pyrazolyl, Imidazolyl, Isoxazolyl, Isothiazolyl, Oxadiazolyl, Thiadiazolyl, Triazolyl, Tetrazolyl, N-Oxidopyridyl, Pyrimidinyl, N-Oxidopyrimidinyl, Pyridazinyl, Pyrazinyl, N-Oxidopyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxatriazinyl, Tetrazo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl besteht, wobei der Heterocyclus gegebenenfalls durch 1 bis 5 Substituenten substituiert ist, welche aus der Gruppe ausgewählt sind, die aus

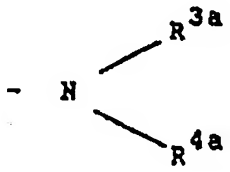
(i) C_{1-4}-Alkyl

(ii) C_{3-6}-Cycloalkyl

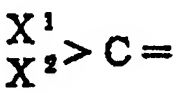
(iii) C_{6-10}-Aryl

(iv) C_{1-4}-Alkoxy
(v) C_{3-6}-Cycloalkyloxy
(vi) C_{6-10}-Aryloxy
(vii) C_{7-12}-Aralkyloxy
(viii) C_{1-4}-Alkylthio
(ix) C_{3-6}-Cycloalkylthio
(x) C_{6-10}-Arylthio
(xi) C_{7-12}-Aralkylthio
(xii) Mono-C_{1-4}-alkylamino
(xiii) Di-C_{1-4}-alkylamino
(xiv) C_{3-6}-Cycloalkylamino
(xv) C_{6-10}-Arylamino
(xvi) C_{7-12}-Aralkylamino
(xvii) Halogen
(xviii) C_{1-4}-Alkoxycarbonyl
(xix) C_{6-10}-Aryloxycarbonyl
(xx) C_{3-6}-Cycloalkyloxycarbonyl
(xxi) C_{7-12}-Aralkyloxycarbonyl
(xxii) C_{1-5}-Alkanoyl
(xxiii) C_{1-15}-Alkanoyloxy
(xxiv) Carbamoyl, N-Methylcarbamoyl, N,N-Dimethylcarbamoyl, N-Ethylcarbamoyl, N,N-Diethylcarbamoyl, N-Phenylcarbamoyl, Pyrrolidinocarbamoyl, Piperidinocarbamoyl, Piperazinocarbamoyl, Morpholinocarbamoyl oder N-Benzylcarbamoyl,
(xxv) N-Methylcarbamoyloxy, N,N-Dimethylcarbamoyloxy, N-Ethylcarbamoyloxy, N-Benzylcarbamoyloxy, N,N-Dibenzylcarbamoyloxy oder N-Phenylcarbamoyloxy,
(xxvi) C_{1-4}-Alkanoylamino,
(xxvii) C_{6-10}-Arylcarbonylamino,
(xxviii) C_{1-4}-Alkoxycarbonylamino,
(xxix) C_{7-12}-Aralkyloxycarbonyl,
(xxx) Methansulfonylamino, Ethansulfonylamino, Butansulfonylamino, Benzolsulfonylamino, Toluolsulfonylamino, Naphthalinsulfonylamino, Trifluormethansulfonylamino, 2-Chlorethansulfonylamino oder 2,2,2-Trifluormethansulfonylamino,
(xxxi) Pyrrolidinyl, Pyrrolyl, Pyrazolyl, Imidazolyl, Furyl, Thienyl, Oxazolyl, Isoxazolyl, Isothiazolyl, Thiazolyl, Piperidinyl, Pyridyl, Piperazinyl, Pyrimidinyl, Pyranyl, Tetrahydropyranyl, Tetrahydrofuryl, Indolyl, Chinolyl, 1,3,4-Oxadiazolyl, Thieno[2,3-d]pyridyl, 1,2,3-Thiadiazolyl, 1,3,4-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1,3,4-Triazolyl, Tetrazolyl, 4,5-Dihydro1,3-dioxazolyl, Tetrazolo[1,5-b]-pyridazinyl, Benzothiazolyl, Benzoxazolyl, Benzimidazolyl oder Benzothienyl,
(xxxii) einer Heterocyclylthio-, Heterocyclyloxy-, Heterocyclylamino- oder Heterocyclylcarbonylaminogruppe, welche aus dem Binden irgendeiner der vorstehend definierten heterocyclischen Gruppen (xxxi) an das S-, O-, N-Atom oder eine Carbonylaminogruppe stammt,
(xxxiii) Di-C_{1-4}-alkylphosphinothioylamino,
(xxxiv) Methoxyimino, Ethoxyimino, 2-Fluorethoxyimino, Carboxymethoxyimino, 1-Carboxy-1-methylethoxylmino, 2,2,2-Trichlorethoxycarbonylmethoxyimino, 1-(2,2,2-Trichlorethoxycarbonyl)-1-methylethoxyimino, (2-Aminothiazol-4-yl)methoxyimino oder (1H-Imidazol-4-yl)methoxyimino,
(xxxv) C_{1-4}-Alkylsulfonyloxy,
(xxxvi) C_{6-10}-Arylsulfonyloxy,
(xxxvii) Di-C_{6-10}-arylphosphinothioylamino,
(xxxviii) Thiocarbamoylthio, N-Methylthiocarbamoylthio, N,N-Dimethylthiocarbamoylthio, N-Ethylthiocarbamoylthio, N-Benzylthiocarbamoylthio, N,N-Dibenzylthiocarbamoylthio oder N-Phenylthiocarbamoylthio,
(xxxix) Trimethylsilyloxy, t-Butyldimethylsilyloxy, t-Butyldiphenylsilyloxy oder Dimethylphenylsilyloxy,
(xL) Trimethylsilyl, t-Butyldimethylsilyl, t-Butyldiphenylsilyl oder Dimethylphenylsilyl,
(xLi) C_{1-4}-Alkylsulfinyl,
(xLii) C_{6-10}-Arylsulfinyl,
(xLiii) C_{1-4}-Alkylsulfonyl,
(xLiv) C_{6-10}-Arylsulfonyl,
(xLv) C_{1-4}-Alkoxycarbonyloxy,
(xLvi) Halogen-C_{1-4}-alkyl,

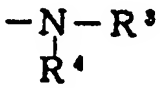
(xLvii) Halogen-C_{1-4}-alkoxy, Halogen-C_{1-4}-alkylthio, Halogen-C_{1-4}-alkylsulfinyl oder Halogen-C_{1-4}-alkylsulfonyl,
(xLviii) Cyano, Nitro, Hydroxyl, Carboxyl, Sulfo, Phosphono,
(xLix) C_{1-4}-Alkyloxysulfonyl,
(L) C_{6-10}-Aryloxysulfonyl,
(Li) C_{7-12}-Aralkyloxysulfonyl und
(Lii) einer Di-C_{1-4}-alkyloxyphosphorylgruppe besteht,
mit der Maßgabe, daß wenn R^2 ein Wasserstoffatom ist, R^1 eine Gruppe der Formel



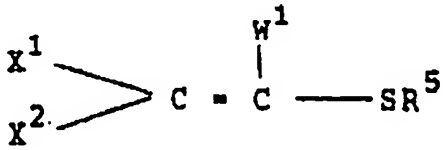
ist [worin R^{3a} Wasserstoff, C_{1-4}-Alkyl, C_{7-9}-Phenylalkyl oder C_{1-4}-Alkanoyl ist und R^{4a} Wasserstoff, C_{1-4}-Alkyl, C_{1-4}-Alkoxy-C_{1-4}-alkyl, (Di-C_{1-4}-alkylamino)-C_{1-4}-alkyl,Tri-C_{1-4}-alkylsilyl-C_{1-4}-alkyl,C_{2-4}-Alkenyl oder Pyridyl- oder Thiazolyl-C_{1-2}-alkyl ist, worin der Pyridyl- oder Thiazolylteil gegebenenfalls mit einem Halogenatom substituiert sein kann, oder R^{3a} und R^{4a} mit dem benachbarten Stickstoffatom zusammengenommen Pyrrolidino bilden] und A• Pyridyl, Pyrazinyl oder Thiazolyl ist, wovon jedes gegebenenfalls mit einem Halogen, C_{1-4}-Alkyl, C_{1-4}-Alkylthio oder C_{1-4}-Alkoxy substituiert sein kann, und mit der Maßgabe, daß wenn



O_2N-CH= ist,
R^1



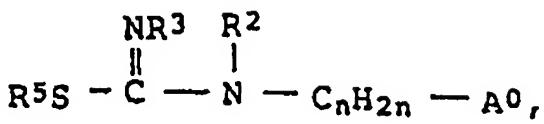
ist,
R^3 Wasserstoff, C_{1-5}-Alkyl oder C_{3-6}-Cycloalkyl ist,
R^4 Wasserstoff, C_{1-5}-Alkyl, C_{3-6}-Cycloalkyl, Benzyl oder Pyrimidinylmethyl ist, oder
R^3 und R^4 zusammen mit dem benachbarten Stickstoffatom eine cyclische Aminogruppe Pyrrolidinyl oder Piperazinyl bilden und
R^2 Wasserstoff, C_{1-5}-Alkyl oder C_{3-6}-Cycloalkyl ist,
A• kein durch C_{1-4}-Halogenalkyl, C_{1-4}-Halogenalkoxy, C_{1-4}-Halogenalkylthio, C_{1-4}-Halogenalkylsulfinyl, C_{1-4}-Halogenalkylsulfonyl, Cyano, Nitro oder Hydroxyl substituiertes Pyridyl ist,
oder eines Salz derselben,
welches das
(1) Umsetzen einer Verbindung der Formel

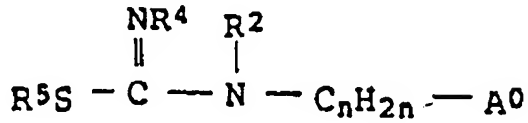


oder eines Salzes derselben mit einer Verbindung der Formel

Y - W^2

oder einem Salz derselben, oder
(2) Umsetzen einer Verbindung der Formel





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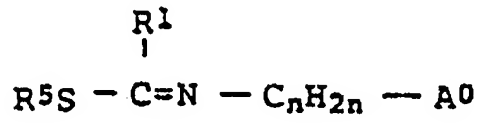
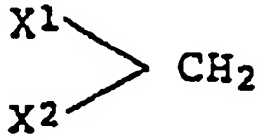
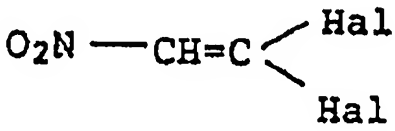


oder eines Salzes derselben mit einer Verbindung der Formel



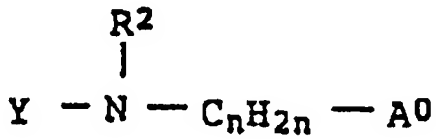
oder einem Salz derselben, oder
(3) Umsetzen einer Verbindung der Formel



oder

O_2N - $CH_2C(Hal)_3$

(i) mit einer Verbindung der Formel



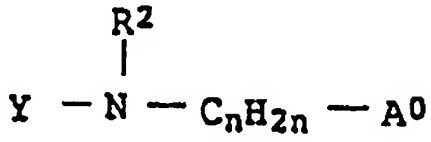
oder einem Salz derselben und anschließend das Umsetzen des sich daraus ergebenden Produkts mit einer Verbindung der Formel

R^1 - Y

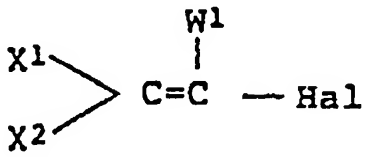
oder einem Salz derselben, oder (ii) mit einer Verbindung der Formel

$R^1 - Y$

oder einem Salz derselben und anschließend das Umsetzen des sich daraus ergebenden Produkts mit einer Verbindung der Formel



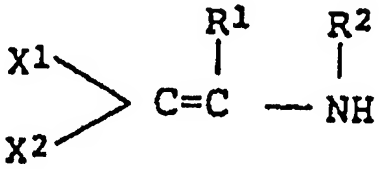
oder einem Salz derselben, oder
(4) Umsetzen einer Verbindung der Formel



oder eines Salzes derselben mit einer Verbindung der Formel

$Y - W^2$

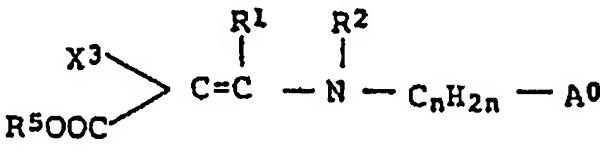
oder einem Salz derselben, oder
(5) Umsetzen einer Verbindung der Formel



oder eines Salzes derselben mit einer Verbindung der Formel

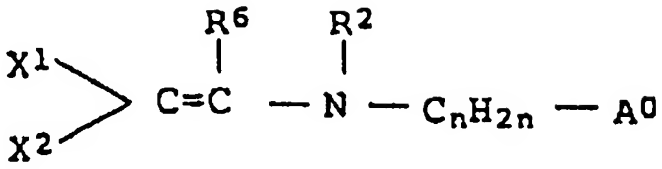
$A^{\circ} - C_nH_{2n} - Hal$

oder einem Salz derselben, oder
(6) Unterziehen einer Verbindung der Formel

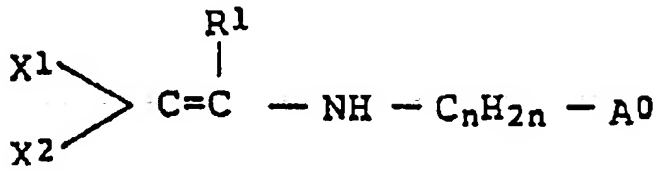


oder eines Salzes derselben einer Hydrolysereaktion und anschließend einer Decarboxylierungsreaktion, oder

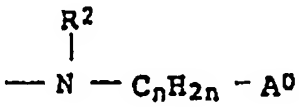
(7) Unterziehen einer Verbindung der Formel



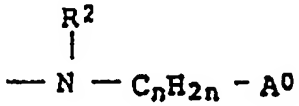
oder



oder eines Salzes derselben der Alkylierung, Acylierung, Alkoxycarbonylierung, Sulfonylierung oder Phosphorylierung, in welchen Formeln R^5 C_{1-4}-Alkyl oder Aralkyl ist; wenn W^1

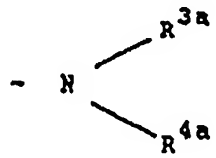


ist, W^2 R^1 ist und wenn W^1 R^1 ist, W^2



ist; Y ein Wasserstoffatom oder ein Alkalimetall ist; R^3 ein Wasserstoffatom, Alkyl, Aryl, Aralkyl, Heterocyclyl, Acyl, Alkoxycarbonyl, Aryloxycarbonyl, Heterocyclyloxycarbonyl, Arylsulfonyl, Alkylsulfonyl, Dialkoxyphosphoryl, Alkoxy, Hydroxyl, Amino, Dialkylamino, Acylamino, Alkoxycarbonylamino, Alkylsulfonylamino, Dialkoxyphosphorylamino, Aralkyloxy oder Alkoxycarbonylalkyl ist; R^4 ein Wasserstoffatom oder Alkyl, Cycloalkyl, Alkenyl, Cycloalkenyl oder Alkinyl, welche Gruppen gegebenenfalls substituiert sein können, oder Pyridyl- oder Thiazolyl-C_{1-2}-alkyl ist, worin der Pyridyl- und Thiazolylteil gegebenenfalls mit einem Halogenatom substituiert sein kann; Hal ein Halogenatom ist; X^3 eine elektronenanziehende Gruppe ist; R^6 eine über ein Stickstoffatom gebundene Gruppe ist, welche wenigstens ein Wasserstoffatom enthält und X^1, X^2, R^1, R^2, n und A• wie in Anspruch 1 definiert sind, umfaßt.

2. Verfahren wie in Anspruch 1 beansprucht, bei welchem R^2 Wasserstoff ist, R^1 eine Gruppe der Formel



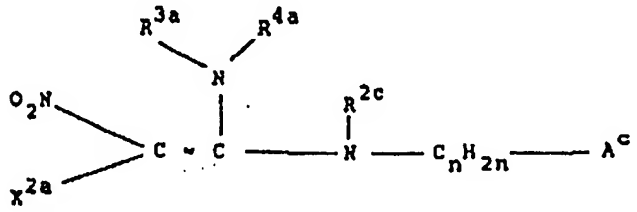
ist (worin R^{3a} und R^{4a} wie in Anspruch 1 definiert sind) und A• ein aus der Klasse ausgewählter Heterocyclus ist, welche aus Pyridyl, Pyrazinyl und Thiazolyl besteht, wobei der unmittelbar voranstehend für A• angeführte Heterocyclus gegebenenfalls mit Halogen, C_{1-4}-Alkyl, C_{1-4}-Alkylthio oder C_{1-4}-Alkoxy substituiert ist.

3. Verfahren wie in Anspruch 1 beansprucht, bei welchem R^2 von Wasserstoff verschieden ist.

4. Verfahren wie in Anspruch 1 beansprucht, bei welchem
X^1 Nitro ist,
X^2 Wasserstoff, C_{1-2}-Alkoxycarbonyl oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^1 Amino, Mono- oder Di-C_{1-4}-alkylamino, Halogen-C_{1-4}-alkylamino, N-C_{1-4}-Alkyl-N-C_{1-2}-alkanoylamino, N-Halogen-C_{1-4}-alkyl-N-C_{1-2}-alkanoylamino oder C_{1-2}-Alkanoylamino ist,
R^2 Wasserstoff, C_{1-2}-Alkoxy, Di-C_{1-2}-alkylamino, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl oder C_{1-2}-Alkanoyl ist,
n 0 oder 1 ist,
A* 2- oder 3-Thienyl, 2- oder 3-Furyl, 2- oder 3-Pyrrolyl, 2-, 3- oder 4-Pyridyl, 2-, 4- oder 5-Oxazolyl, 2-, 4- oder 5-Thiazolyl, 3-, 4- oder 5-Pyrazolyl, 2-, 4- oder 5-Imidazolyl, 3-, 4-oder 5-Isoxazolyl, 3-, 4- oder 5-Isothiazolyl, 3- oder 5-(1,2,4-Oxadiazolyl), 1,3,4-Oxadiazolyl, 3- oder 5-(1,2,4-Thiadiazolyl), 1,3,4-Thiadiazolyl, 4- oder 5-(1,2,3-Thiadiazolyl), 1,2,5-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1H- oder 2H-Tetrazolyl, N-Oxido-2-, 3- oder 4-pyridyl, 2-, 4- oder 5-Pyrimidinyl, N-Oxido-2-, 4- oder 5-pyrimidinyl, 3- oder 4-Pyridazinyl, Pyrazinyl, N-Oxido-3- oder 4-pyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl oder Phenoxazinyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl, C_{1-4}-Alkoxy, Halogen-C_{1-4}-alkoxy, C_{1-4}-Alkylthio oder Halogen-C_{1-4}-alkylthio substituiert sein kann, oder eines Salzes derselben.

5. Verfahren wie in Anspruch 1 beansprucht, bei welchem
X^1 Nitro ist,
X^2 Wasserstoff oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^1 Amino, Mono- oder Di-C_{1-2}-alkylamino, Halogen-C_{1-2}-alkylamino, N-C_{1-2}-Alkyl-N-C_{1-2}-alkanoylamino, N-Halogen-C_{1-2}-alkyl-N-C_{1-2}-alkanoylamino oder C_{1-2}-Alkanoylamino ist,
R^2 Wasserstoff, C_{1-2}-Alkoxy, Di-C_{1-2}-alkylamino, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl oder C_{1-2}-Alkanoyl ist,
n 1 ist, und
A* Pyridyl, Pyrazinyl oder Thiazolyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl, Halogen-C_{1-4}-alkyl, C_{1-4}-Alkoxy, Halogen-C_{1-4}-alkoxy, C_{1-4}-Alkylthio oder Halogen-C_{1-4}-alkylthio substituiert sein kann, oder eines Salzes derselben.

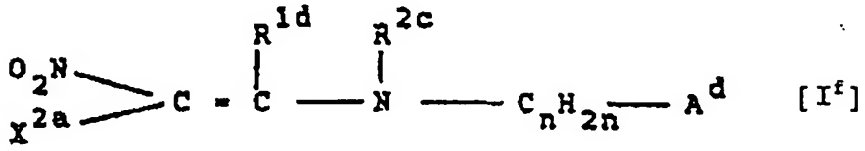
6. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung der Formel



[I^e]

worin
X^{2a} Wasserstoff, C_{1-4}-Alkoxycarbonyl oder C_{1-4}-Alkylsulfonylthiocarbamoyl ist,
R^{2c} Wasserstoff, C_{1-3}-Alkanoyl, C_{1-4}-Alkyl, Mono- oder Di-C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{7-9}-Aralkyl, Mono- oder Di-C_{1-4}-alkylamino oder C_{1-4}-Alkoxy ist,
A^c 3- oder 4-Pyridyl, Pyrazinyl oder 4- oder 5-Thiazolyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl oder C_{1-4}-Alkoxy substituiert sein kann,
n 1 ist und
R^{3a} und R^{4a} wie in Anspruch 1 definiert sind, oder eines Salzes derselben.

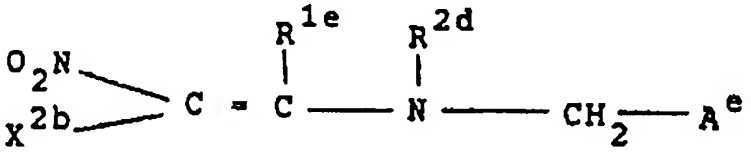
7. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung der Formel



[I^f]

ist, worin
X^{2a} Wasserstoff, C_{1-4}-Alkoxycarbonyl oder C_{1-4}-Alkylsulfonylthiocarbamoyl ist,
R^{1d} Amino, Mono- oder Di-C_{1-4}-alkylamino, N-C_{1-4}-Alkyl-N-C_{1-3}-alkanoylamino C_{7-9}-Aralkylamino, Halogenthiazolyl-C_{1-2}-alkylamino oder C_{1-4}-Alkoxy-C_{1-2}-alkylamino ist,
R^{2c} Wasserstoff, C_{1-3}-Alkanoyl, C_{1-4}-Alkyl, Mono- oder Di-C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{7-9}-Aralkyl, Mono- oder Di-C_{1-4}-alkylamino oder C_{1-4}-Alkoxy ist,
n 0, 1 oder 2 ist und
A^d 3- oder 4-Pyridyl, Pyrazinyl oder 5-Thiazolyl ist, wovon jedes gegebenenfalls mit Halogen, C_{1-4}-Alkyl oder C_{1-4}-Alkoxy substituiert sein kann, oder eines Salzes derselben.

8. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung der Formel

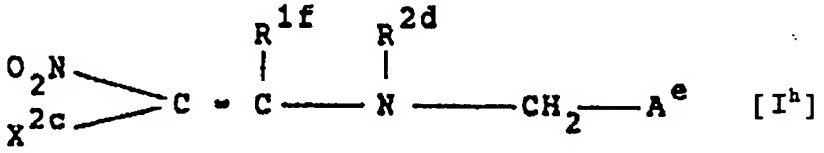


[I^g]

ist, worin
X^{2b} Wasserstoff oder C_{1-2}-Alkylsulfonylthiocarbamoyl ist,
R^{1e} Amino, Mono- oder Di-C_{1-2}-alkylamino oder N-C_{1-2}-Alkyl-N-formylamino,
R^{2d} Wasserstoff, C_{1-2}-Alkyl oder C_{1-3}-Alkanoyl ist und
A^e eine Gruppe der Formel

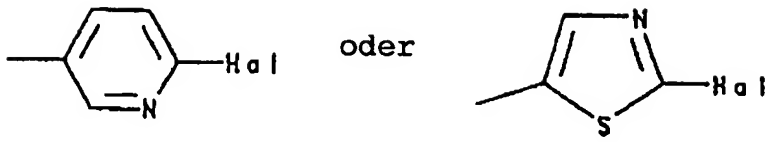
ist, worin Hal ein Halogenatom ist, oder eines Salzes derselben.

9. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung der Formel



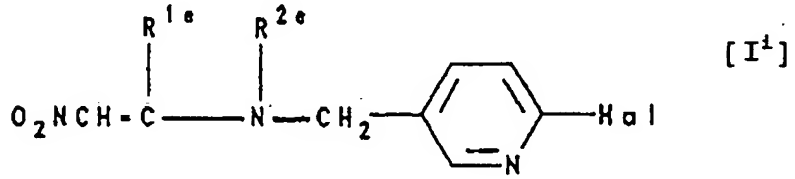
[I^h]

ist, worin
X^{2c} Wasserstoff oder Methylsulfonylthiocarbamoyl ist,
R^{1f} Amino, Methylamino, Dimethylamino oder N-Methyl-N-formylamino ist,
R^{2d} ein Wasserstoffatom, Formyl oder C_{1-2}-Alkyl ist und
A^e eine Gruppe der Formel



ist, worin Hal ein Halogenatom ist, oder eines Salzes derselben.

10. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung der Formel



[I^i]

ist, worin
R^{1e} Amino, Mono- oder Di-C_{1-2}-alkylamino oder N-C_{1-2}-Alkyl-N-formylamino ist,
R^{2e} C_{1-2}-Alkyl oder Formyl ist und
Hal ein Halogenatom ist, oder eines Salzes derselben.

11. Verfahren wie in Anspruch 1 beansprucht, wobei der Heterocyclus aus der folgenden Gruppe ausgewählt ist und gegebenenfalls wie in Anspruch 1 definiert substituiert ist, wobei die Gruppe aus 2- oder 3-Thienyl, 2- oder 3-Furyl, 2- oder 3-Pyrrolyl, 2-, 4- oder 5-Oxazolyl, 2-, 4- oder 5-Thiazolyl, 3-, 4-oder 5-Pyrazolyl, 2-, 4- oder 5-Imidazolyl, 3-, 4- oder 5-Isoxazolyl, 3-, 4- oder 5-Isothiazolyl, 3- oder 5-(1,2,4-Oxadiazolyl), 1,3,4-Oxadiazolyl, 3- oder 5-(1,2,4-Thiadiazolyl), 1,3,4-Thiadiazolyl, 4- oder 5-(1,2,3-Thiadiazolyl), 1,2,5-Thiadiazolyl, 1,2,3-Triazolyl, 1,2,4-Triazolyl, 1H- oder 2H-Tetrazolyl, N-Oxido-2-, 3- oder 4-pyridyl, 2-, 4- oder 5-Pyrimidinyl, N-Oxido-2-, 4- oder 5-pyrimidinyl, 3- oder 4-Pyridazinyl, Pyrazinyl, N-Oxido-3- oder 4-pyridazinyl, Benzofuryl, Benzothiazolyl, Benzoxazolyl, Triazinyl, Oxotriazinyl, Tetrazolo[1,5-b]pyridazinyl, Triazolo[4,5-b]pyridazinyl, Oxoimidazinyl, Dioxotriazinyl, Pyrrolidinyl, Piperidinyl, Pyranyl, Thiopyranyl, 1,4-Oxazinyl, Morpholinyl, 1,4-Thiazinyl, 1,3-Thiazinyl, Piperazinyl, Benzimidazolyl, Chinolyl, Isochinolyl, Cinnolinyl, Phthalazinyl, Chinazolinyl, Chinoxalinyl, Indolizinyl, Chinolizinyl, 1,8-Naphthyridinyl, Purinyl, Pteridinyl, Dibenzofuranyl, Carbazolyl, Acridinyl, Phenanthridinyl, Phenazinyl, Phenothiazinyl und Phenoxazinyl besteht.

12. Verfahren wie in Anspruch 1 beansprucht zum Herstellen einer Verbindung, welche aus 1-[N-(6-Chlor-3-pyridylmethyl)-N-methyl]amino-1-methylamino-2-nitroethylen, 1-(6-Chlor-3-pyridylmethyl)amino-1-dimethylamino-2-nitroethylen und 1-[N-(6-Chlor-3-pyridylmethyl)-N-ethyl]amino-1-methylamino-2-nitroethylen ausgewählt ist.

13. Verfahren zum Herstellen einer insektiziden/milbiziden Zusammensetzung, welche das Mischen einer insektizid/milbizid wirksamen Menge wenigstens eines der gemäß einem der Ansprüche 1 bis 12 hergestellten α-ungesättigten Amine oder eines Salzes derselben zusammen mit einem geeigneten Träger oder Trägern umfaßt.

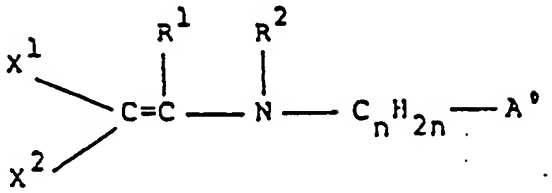
14. Verfahren zum Bekämpfen unerwünschter Insekten oder Milben, welches das Aufbringen einer insektizid oder milbizid wirksamen Menge der gemäß einem der Ansprüche 1 bis 12 hergestellten Verbindung der Formel [I•] oder eines Salzes derselben auf die Insekten oder Milben oder ihren Lebensraum umfaßt.

15. Verfahren des Anspruchs 14, bei welchem die Verbindung oder das Salz in einer Zusammensetzung der Verbindung oder des Salzes mit einem geeigneten Träger oder Trägern angewandt wird.

Revendications

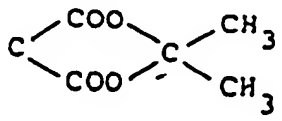
Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Amine α-insaturée de formule :



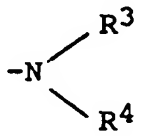
(I⁰)

dans laquelle
l'un des X^1 et X^2 représente un groupe électro-attracteur et l'autre représente un atome d'hydrogène ou un groupe électro-attracteur, ledit groupe électro-attracteur étant un groupe cyano, nitro, (alcoxy en C_{1-4})-carbonyle, carboxy, (aryloxy en C_{6-10})-carbonyle, hétérocycle-oxycarbonyle, alkylsulfonyle en C_{1-4} qui peut être substitué par un atome d'halogène, aminosulfonyle, di-(alcoxy en C_{1-4})-phosphoryle, alcanoyle en C_{1-4} qui peut être substitué par un atome d'halogène, (alkyle en C_{1-4})-sulfonylthiocarbamoyle ou carbamoyle, ou encore un atome d'halogène, ou bien X^1 et X^2, conjointement avec l'atome de carbone auquel ils sont liés, forment un cycle de formule

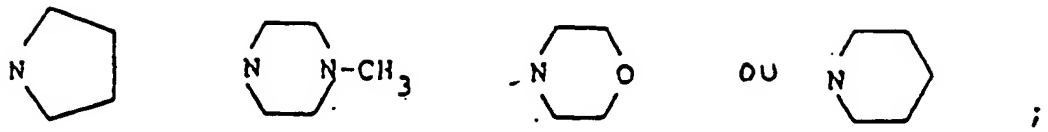


;

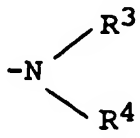
R^1 représente un groupe de formule



dans laquelle
R^3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-20}, aryle en C_{6-10}, aralkyle en C_{7-9}, hétérocyclique, alcanoyle en C_{1-4}, (aryle en C_{6-10})-carbonyle, (alcoxy en C_{1-4})-carbonyle, (aryloxy en C_{6-10})-carbonyle, hétérocycleoxy-carbonyle, arylsulfonyle en C_{6-10}, alkylsulfonyle en C_{1-4}, di-(alcoxy en C_{1-4})-phosphoryle, alcoxy en C_{1-4}, hydroxy, amino, di-(alkyle en C_{1-4})-amino, alcanoylamino en C_{1-4}, (alcoxy en C_{1-4})-carbonylamino, alkylsulfonylamino en C_{1-4}, di-(alcoxy en C_{1-4})-phosphorylamino, aralkyloxy en C_{7-9} ou (alcoxy en C_{1-4})-carbonyl-(alkyle en C_{1-4}) ; et
R^4 représente un atome d'hydrogène ou un groupe alkyle en C_{1-20}, cycloalkyle en C_{3-6}, alcényle en C_{2-6}, cycloalcényle en C_{3-6} ou alcynyle en C_{2-6}, chacun des radicaux définis pour R^4, à l'exception de l'atome d'hydrogène, pouvant éventuellement porter de 1 à 3 substituants, choisis dans l'ensemble constitué par les atomes d'halogène et les groupes hydroxy, alcoxy en C_{1-4}, di-(alkyle en C_{1-4})-amino, alkylthio en C_{1-4}, alcanoylamino en C_{1-3}, alkylsulfonylamino en C_{1-4}, tri-(alkyle en C_{1-4})-silyle, pyridyle et thiazolyle, les groupes pyridyle et thiazolyle pouvant chacun être encore substitués par des atomes d'halogène ; ou bien
R^3 et R^4, conjointement avec l'atome d'azote adjacent, forment un groupe aminocyclique de formule :



R^2 représente (1) un atome d'hydrogène, (2) un groupe lié par un atome de carbone et choisi dans l'ensemble constitué par les groupes alcanoyle en C_{1-4}, alkyle en C_{1-20}, alcényle en C_{2-6}, cycloalkyle en C_{3-6}, aryle en C_{6-10}, aralkyle en C_{7-9}, 3-pyridyle et 4-pyridyle, ce groupe lié par un atome de carbone portant éventuellement de 1 à 3 substituants choisis dans l'ensemble constitué par les groupes alkylthio en C_{1-4}, alcoxy en C_{1-4}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, (alcoxy en C_{1-4})-carbonyle, alkylsulfonyle en C_{1-4} et alcanoyle en C_{1-4}, ainsi que par les atomes d'halogène, (3) un groupe lié par un atome d'oxygène et choisi dans l'ensemble constitué par les groupes, alcoxy en C_{1-4}, cycloalcoxy en C_{3-6}, alcényloxy en C_{2-4}, cycloalcényloxy en C_{3-6}, éthynyloxy, aryloxy en C_{6-10}, thiényloxy et hydroxy, ce groupe lié par un atome d'oxygène pouvant éventuellement porter de 1 à 3 substituants choisis dans l'ensemble constitué par les atomes d'halogène et le groupe phényle, ou (4) un groupe lié par un atome d'azote, de formule :

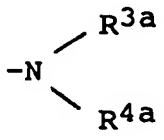


dans laquelle R^3 et R^4 ont les significations indiquées plus haut ;
n représente un nombre entier valant 0, 1 ou 2 ;
A^0 représente un hétérocycle ;
l'hétérocycle dudit groupe hétérocycle-carbonyle indiqué à propos de X_1 et X_2, ledit hétérocycle indiqué à propos de R^3, l'hétérocycle dudit groupe hétérocycle-oxycarbonyle indiqué à propos de R^3, et ledit hétérocycle indiqué pour A^0 étant chacun un élément choisi dans l'ensemble constitué par les groupes thiényle, furyle, pyrrolyle, pyridyle, oxazolyle, thiazolyle, pyrazolyle, imidazolyle, isoxazolyle, isothiazolyle, oxadiazolyle, thiadiazolyle, triazolyle, tétrazolyle, N-oxydopyridyle, pyrimidinyle, N-oxydopyrimidinyle, pyridazinyle, pyrazinyle, N-oxydopyridazinyle, benzofuryle, benzothiazolyle, benzoxazolyle, triazinyle, oxotriazinyle, tétrazo[1,5-b]pyridazinyle, triazolo[4,5-b]pyridazinyle, oxoimidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle et phénoxazinyle, ledit hétérocycle pouvant éventuellement porter de 1 à 5 substituants choisis dans l'ensemble constitué de :

(I) alkyle en C_{1-4}
(II) cycloalkyle en C_{3-6}
(III) aryle en C_{6-10}
(IV) alcoxy en C_{1-4}
(V) cycloalkyloxy en C_{3-6}
(VI) aryloxy en C_{6-10}
(VII) aralcoxy en C_{7-12}
(VIII) alkylthio en C_{1-4}
(IX) cycloalkylthio en C_{3-6}
(X) arylthio en C_{6-10}
(XI) aralkylthio en C_{7-12}
(XII) mono-(alkyle en C_{1-4})-amino
(XIII) di-(alkyle en C_{1-4})-amino
(XIV) cycloalkylamino en C_{3-6}
(XV) arylamino en C_{6-10}
(XVI) aralkylamino en C_{7-12}
(XVII) halogéno
(XVIII) (alcoxy en C_{1-4})-carbonyle

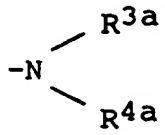
(XIX) (aryloxy en C_{6-10})-carbonyle
(XX) (cycloalkyloxy en C_{3-6})-carbonyle
(XXI) (aralkyloxy en C_{7-12})-carbonyle
(XXII) alcanoyle en C_{1-5}
(XXIII) alcanoyloxy en C_{1-15}
(XXIV) carbamoyle, N-méthylcarbamoyle, N,N-diméthylcarbamoyle, N-éthylcarbamoyle, N,N-diéthylcarbamoyle, N-phénylcarbamoyle, pyrrolidinocarbamoyle, pipéridinocarbamoyle, pipérazinocarbamoyle, morpholinocarbamoyle ou N-benzylcarbamoyle
(XXV) N-méthylcarbamoyloxy, N,N-diméthylcarbamoyloxy, N-éthylcarbamoyloxy, N-benzylcarbamoyloxy, N,N-dibenzylcarbamoyloxy ou N-phénylcarbamoyloxy
(XXVI) alcanoylamino en C_{1-4}
(XXVII) (aryle en C_{6-10})-carbonylamino
(XXVIII) (alcoxy en C_{1-4})-carbonylamino
(XXIX) (aralcoxy en C_{7-12})-carbonyle
(XXX) méthanesulfonylamino, éthanesulfonylamino, butanesulfonylamino, benzènesulfonylamino, toluènesulfonylamino, naphtalènesulfonylamino, trifluorométhanesulfonylamino, 2-chloroéthanesulfonylamino ou 2,2,2-trifluoroéthanesulfonylamino
(XXXI) pyrrolidinyle, pyrrolyle, pyrazolyle, imidazolyle, furyle, thiényle, oxazolyle, isoxazolyle, isothiazolyle, thiazolyle, pipéridinyle, pyridyle, pipérazinyle, pyrimidinyle, pyranyle, tétrahydropyranyle, tétrahydrofuryle, indolyle, quinolyle, 1,3,4-oxadiazolyle, thiéno[2,3-d]pyridyle, 1,2,3-thiadiazolyle, 1,3,4-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1,3,4-triazolyle, tétrazolyle, 4,5-dihydro-1,3-dioxazolyle, tétrazolo[1,5-b]pyridazinyle, benzothiazolyle, benzoxazolyle, benzimidazolyle ou benzothiényle
(XXXII) les groupes hétérocycle-thio, hétérocycle-oxy, hétérocycle-amino ou hétérocycle-carbonylamino, qui dérivent du rattachement de l'un quelconque des groupes hétérocycliques (XXXI) définis ci-dessus à un atome S, O ou N ou à un groupe carbonylamino
(XXXIII) di-(alkyle en C_{1-4})-phosphinothioylamino
(XXXIV) méthoxyimino, éthoxyimino, 2-fluoroéthoxyimino, carboxyméthoxyimino, 1-carboxy-1-méthyl-éthoxyimino, 2,2,2-trichloroéthoxycarbonyl-méthoxyimino, 1-(2,2,2-trichloroéthoxycarbonyl)-1-méthyl-éthoxyimino, (2-aminothiazol-4-yl)-méthoxyimino ou (1H-imidazol-4-yl)-méthoxyimino
(XXXV) alkylsulfonyloxy en C_{1-4}
(XXXVI) arylsulfonyloxy en C_{6-10}
(XXXVII) di-(aryle en C_{6-10})-phosphinothioylamino
(XXXVIII) thiocarbamoylthio, N-méthyl-thiocarbamoylthio, N,N-diméthyl-thiocarbamoylthio, N-éthyl-thiocarbamoylthio, N-benzyl-thiocarbamoylthio, N,N-dibenzyl-thiocarbamoylthio ou N-phényl-thiocarbamoylthio
(XXXIX) triméthylsilyloxy, t-butyl-diméthylsilyloxy, t-butyl-diphénylsilyloxy ou diméthyl-phénylsilyloxy,
(XL) triméthylsilyle, t-butyl-diméthylsilyle, t-butyldiphénylsilyle ou diméthyl-phénylsilyle
(XLI) alkylsulfinyle en C_{1-4}
(XLII) arylsulfinyle en C_{6-10}
(XLIII) alkylsulfonyle en C_{1-4}
(XLIV) arylsulfonyle en C_{6-10}
(XLV) (alcoxy en C_{1-4})-carbonyloxy
(XLVI) halogénoalkyle en C_{1-4}
(XLVII) halogénoalcoxy en C_{1-4}, halogénoalkylthio en C_{1-4}, halogénoalkylsulfinyle en C_{1-4} ou halogénoalkylsulfonyle en C_{1-4}
(XLVIII) cyano, nitro, hydroxy, carboxy, sulfo, phosphono
(XLIX) alcoxysulfonyle en C_{1-4}
(L) aryloxysulfonyle en C_{6-10}
(LI) aralcoxysulfonyle en C_{7-12}
(LII) di-(alcoxy en C_{1-4})-phosphoryle

sous réserve que, lorsque R^2 représente un atome d'hydrogène, R^1 représente un groupe de formule



dans laquelle R^{3a} représente un atome d'hydrogène ou un groupe alkyle en C_{1-4}, phénylalkyle en C_{7-9} ou alcanoyle en C_{1-4} et R^{4a} représente un atome d'hydrogène ou un groupe alkyle en C_{1-4}, (alcoxy en C_{1-4})-alkyle en C_{1-4}, [di-(alkyle en C_{1-4})-amino]-alkyle en C_{1-4}, tri-(alkyle en C_{1-4})-silyl-alkyle en C_{1-4}, alcényle en C_{2-4}, pyridylalkyle en C_{1-2} ou thiazolyl-alkyle en C_{1-2} le fragment pyridyle ou thiazolyle pouvant éventuellement être substitué par un atome d'halogène, ou bien R^{3a} et R^{4a}, conjointement avec l'atome d'azote adjacent, forment un groupe pyrrolidino,
et A^0 représente un groupe pyridyle, pyrazinyle ou thiazolyle, dont chacun peut éventuellement être substitué par un atome d'halogène ou un groupe alkyle en C_{1-4}, alkylthio en C_{1-4} ou alcoxy en C_{1-4},
et sous réserve que, lorsque $X^1X^2C=$ représente O_2N-CH=, R^1 représente -NR^3R^4, R^3 représentant un atome d'hydrogène ou un groupe alkyle en C_{1-5} ou cycloalkyle en C_{3-6}, R^4 représentant un atome d'hydrogène ou un groupe alkyle en C_{1-5}, cycloalkyle en C_{3-6}, benzyle ou pyrimidinyl-méthyle, ou R^3 et R^4, conjointement avec l'atomed d'azote adjacent, formant un groupe amino cyclique pyrrolidinyle ou pipérazinyle, et R^2 représente un atome d'hydrogène ou un groupe alkyle en C_{1-5} ou cycloalkyle en C_{3-6}, alors A^0 ne représente pas un groupe pyridyle substitué par un groupe halogénoalkyle en C_{1-4}, halogénoalcoxy en C_{1-4}, halogénoalkylthio en C_{1-4}, halogénoalkylsulfinyle en C_{1-4}, halogénoalkylsulfonyle en C_{1-4}, cyano, nitro ou hydroxy ; ou un sel d'un tel composé.

2. Composé conforme à la revendication 1, dans lequel R^2 représente un atome d'hydrogène, R^1 représente un groupe de formule



dans laquelle R^{3a} et R^{4a} ont les définitions indiquées dans la revendication 1, et A^0 représente un hétérocycle choisi dans l'ensemble constitué par les groupes pyridyle, pyrazinyle et thiazolyle, cet hétérocycle que l'on vient de mentionner à propos de A^0 étant éventuellement substitué par un atome d'halogène ou un groupe alkyle en C_{1-4}, alkylthio en C_{1-4} ou alcoxy en C_{1-4}.

3. Composé conforme à la revendication 1, dans lequel R^2 représente autre chose qu'un atome d'hydrogène.

4. Composé conforme à la revendication 1, dans lequel

- X^1 représente un groupe nitro,
- X^2 représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-2})-carbonyle ou (alkyle en C_{1-2})-sulfonylthiocarbamoyle,
- R^1 représente un groupe amino, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, halogéno-(alkyle en C_{1-4})-amino, N-(alkyle en C_{1-4})-N-(alcanoyle en C_{1-2})-amino, N-(halogénoalkyle en C_{1-4})-N-(alcanoyle en C_{1-2})-amino ou (alcanoyle en C_{1-2})-amino,
- R^2 représente un atome d'hydrogène ou un groupe alcoxy en C_{1-2}, di-(alkyle en C_{1-2})-amino, alkyle en C_{1-4}, halogénoalkyle en C_{1-4} ou alcanoyle en C_{1-2},
- n vaut 0 ou 1,
- A^0 représente un groupe 2- ou 3-thiényle, 2- ou 3-furyle, 2- ou 3-pyrrolyle, 2-, 3- ou 4-pyridyle, 2-, 4- ou 5-oxazolyle, 2-, 4- ou 5-thiazolyle, 3-, 4- ou 5-pyrazolyle, 2-, 4- ou 5-imidazolyle, 3-, 4- ou 5-isoxazolyle, 3-, 4- ou 5-isothiazolyle, 3- ou 5-(1,2,4-oxadiazolyle), 1,3,4-oxadiazolyle, 3- ou 5-(1,2,4-thiadiazolyle), 1,3,4-thiadiazolyle, 4- ou 5-(1,2,3-thiadiazolyle), 1,2,5-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1H- ou 2H-tétrazolyle, N-oxydo-2-, 3-ou 4-pyridyle, 2-, 4- ou 5-pyrimidinyle, N-oxydo-2-, 4-ou 5-pyrimidinyle, 3- ou 4-pyridazinyle, pyrazinyle, N-oxydo-3- ou 4-pyridazinyle, benzofuryle, benzothiazolyle, benzoxazolyle, triazinyle, oxotriazinyle, tétrazolo(1,5-b)pyridazinyle, triazolo(4,5-b)pyridazinyle, oxoimidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle, chacun de ces groupes pouvant éventuellement être substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4}, halogénoalkyle en C_{1-4}, alcoxy en C_{1-4},

halogénoalcoxy en C_{1-4}, alkylthio en C_{1-4} ou halogénoalkylthio en C_{1-4},
ou sel d'un tel composé.

5. Composé conforme à la revendication 1, dans lequel

X^1 représente un groupe nitro,

X^2 représente un atome d'hydrogène ou un groupe (alkyle en C_{1-2})-sulfonylthio-carbamoyle,

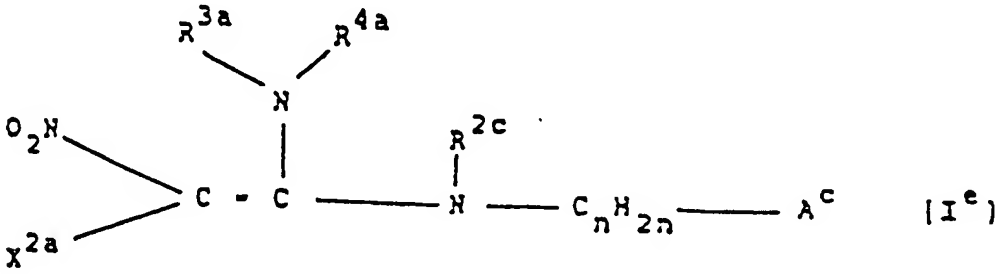
R^1 représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino, halogéno-(alkyle en C_{1-2})-amino, N-(alkyle en C_{1-2})-N-(alcanoyle en C_{1-2})-amino, N-(halogénoalkyle en C_{1-2})-N-(alcanoyle en C_{1-2})-amino ou (alcanoyle en C_{1-2})-amino,

R^2 représente un atome d'hydrogène ou un groupe alcoxy en C_{1-2}, di-(alkyle en C_{1-2})-amino, alkyle en C_{1-4}, halogénoalkyle en C_{1-4} ou alcanoyle en C_{1-2},

n vaut 1, et

A^0 représente un groupe pyridyle, pyrazinyle ou thiazolyle, chacun de ces groupes pouvant éventuellement être substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4}, halogénoalkyle en C_{1-4}, alcoxy en C_{1-4}, halogénoalcoxy en C_{1-4}, alkylthio en C_{1-4} ou halogénoalkylthio en C_{1-4},
ou sel d'un tel composé.

6. Composé conforme à la revendication 1, de formule



$[I^e]$

dans laquelle

X^{2a} représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-4})-carbonyle ou (alkyle en C_{1-4})-sulfonylthiocarbamoyle,

R^{2c} représente un atome d'hydrogène ou un groupe alcanoyle en C_{1-3}, alkyle en C_{1-4}, mono-(alcoxy en C_{1-4})-alkyle en C_{1-4}, di-(alcoxy en C_{1-4})-alkyle en C_{1-4}, aralkyle en C_{7-9}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino ou alcoxy en C_{1-4},

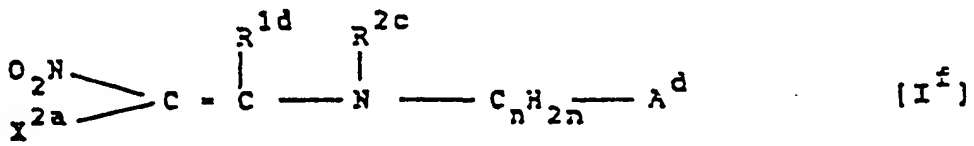
A^c représente un groupe 3-pyridyle, 4-pyridyle, pyrazinyle, 4-thiazolyle ou 5-thiazolyle, chacun de ceux-ci pouvant être éventuellement substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4} ou alcoxy en C_{1-4},

n vaut 1, et

R^{3a} et R^{4a} ont les définitions indiquées dans la revendication 1,

ou un sel d'un tel composé.

7. Composé conforme à la revendication 1, de formule



$[I^f]$

dans laquelle

X^{2a} représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-4})-carbonyle ou (alkyle en C_{1-4})-sulfonylthiocarbamoyle,

R^{1d} représente un groupe amino, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, N-(alkyle en C_{1-4})-N-(alcanoyle en C_{1-3})-amino, aralkylamino en C_{7-9}, halogénothiazolyl-(alkyle en C_{1-2})-amino ou (alcoxy en C_{1-4})-(alkyle en C_{1-2})-amino,

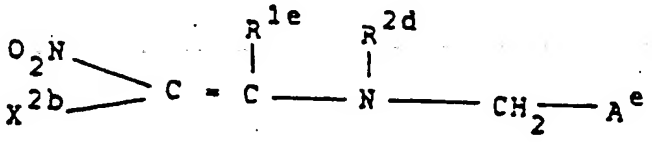
R^{2c} représente un atome d'hydrogène ou un groupe alcanoyle en C_{1-3}, alkyle en C_{1-4}, mono-(alcoxy en C_{1-4})-alkyle en C_{1-4}, di-(alcoxy en C_{1-4})-alkyle en C_{1-4}, aralkyle en C_{7-9}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino ou alcoxy en C_{1-4},

n vaut 0, 1 ou 2, et

A^d représente un groupe 3-pyridyle, 4-pyridyle, pyrazinyle, ou 5-thiazolyle, chacun de ceux-ci pouvant être éventuellement substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4} ou alcoxy en C_{1-4},

ou un sel d'un tel composé.

8. Composé conforme à la revendication 1, qui est un composé de formule



[I^g]

dans laquelle

X^{2b} représente un atome d'hydrogène ou un groupe (alkyle en C_{1-2})-sulfonylthiocarbamoyle,

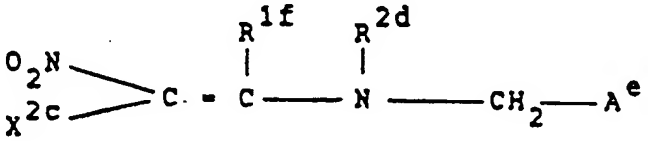
R^{1e} représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino ou N-(alkyle en C_{1-2})-N-formyl-amino,

R^{2d} représente un atome d'hydrogène ou un groupe alkyle en C_{1-2} ou alcanoyle en C_{1-3}, et

A^e représente un groupe de formule

où Hal représente un atome d'halogène,
ou sel d'un tel composé.

9. Composé conforme à la revendication 1, qui est un composé de formule



[I^h]

dans laquelle

X^{2c} représente un atome d'hydrogène ou un groupe méthylsulfonylthiocarbamoyle,

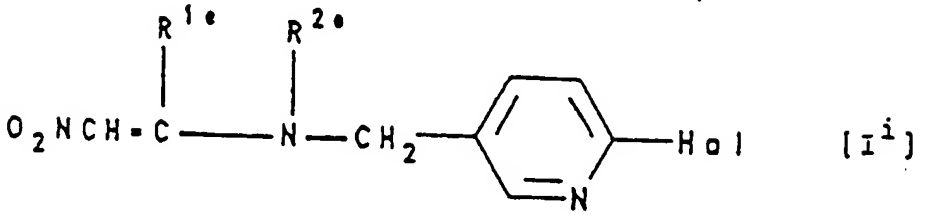
R^{1f} représente un groupe amino, méthylamino, diméthylamino ou N-méthyl-N-formylamino,

R^{2d} représente un atome d'hydrogène ou un groupe formyle ou alkyle en C_{1-2}, et

A^e représente un groupe de formule

où Hal représente un atome d'halogène,
ou sel d'un tel composé.

10. Composé conforme à la revendication 1, qui est un composé de formule



[I^i]

dans laquelle

R^{1e} représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino ou N-(alkyle en C_{1-2})-N-formyl-amino,

R^{2e} représente un groupe alkyle en C_{1-2} ou formyle, et

Hal représente un atome d'halogène,

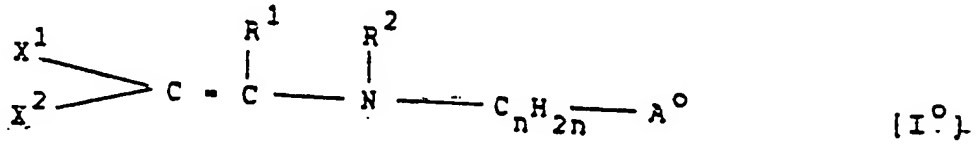
ou sel d'un tel composé.

11. Composé conforme à la revendication 1, dans lequel l'hétérocycle est choisi dans l'ensemble suivant et éventuellement substitué comme indiqué dans la revendication 1, ledit ensemble étant constitué par les groupes 2- ou 3-thiényle, 2- ou 3-furyle, 2- ou 3-pyrrolyle, 2-, 4- ou 5- oxazolyle, 2-, 4- ou 5-thiazolyle, 3-, 4- ou 5-pyrazolyle, 2-, 4- ou 5-imidazolyle, 3-, 4- ou 5-isoxazolyle, 3-, 4- ou 5-isothiazolyle, 3- ou 5-(1,2,4-oxadiazolyle), 1,3,4-oxadiazolyle, 3- ou 5-(1,2,4-thiadiazolyle), 1,3,4-thiadiazolyle, 4- ou 5-(1,2,3-thiadiazolyle), 1,2,5-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1H- ou 2H-tétrazolyle, N-oxydo-2-, 3- ou 4-pyridyle, 2-, 4- ou 5-pyrimidinyle, N-oxydo-2-, 4- ou 5-pyrimidinyle, 3- ou 4-pyridazinyle, pyrazinyle, N-oxydo-3- ou 4-pyridazinyle, benzofuryle, benzo-thiazolyle, benzoxazolyle, triazinyle, oxo-triazinyle, tétrazolo(1,5-b)pyridazinyle, triazolo(4,5-b)pyridazinyle, oxo-imidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle.

12. Composé conforme à la revendication 1, choisi parmi le 1-[N-(6-chloro-3-pyridylméthyl)-N-méthyl]-amino-1-méthylamino-2-nitroéthylène, le 1-(6-chloro-3-pyridyl-méthyl)amino-1-diméthylamino-2-nitro-éthylène, et le 1-[N-(6-chloro-3-pyridylméthyl)-N-éthyl]amino-1-méthylamino-2-nitroéthylène.

13. Composition insecticide/acaricide, qui comprend une quantité efficace insecticide/acaricide d'au moins l'une des amines α-insaturées conformes à l'une quelconque des revendications 1 à 12, ou un sel d'une telle amine, conjointement avec un ou des véhicules appropriés.

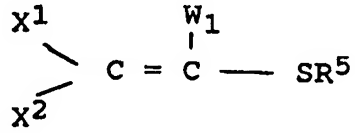
14. Procédé de préparation d'une amine α-insaturée de formule



[I^o]

dans laquelle les symboles ont les définitions indiquées dans la revendication 1, ou d'un sel d'une telle amine, ledit procédé comprenant :

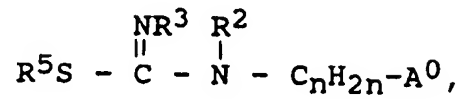
(1) la réaction d'un composé de formule

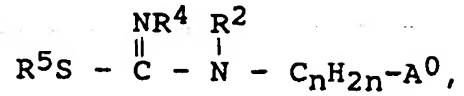


ou d'un sel d'un tel composé avec un composé de formule

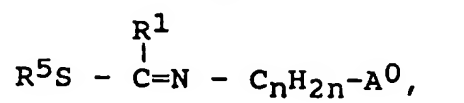
$Y - W^2$

ou un sel d'un tel composé, ou
(2) la réaction d'un composé de formule

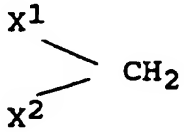




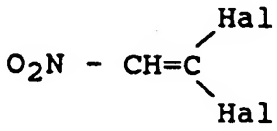
ou



ou d'un sel d'un tel composé, avec un composé de formule



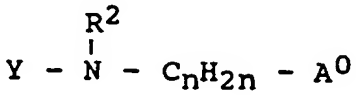
ou un sel d'un tel composé, ou
(3) la réaction d'un composé de formule



ou

$O_2N - CH_2C(Hal)_3$

(a) avec un composé de formule



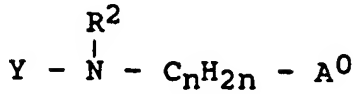
ou un sel d'un tel composé, puis la réaction du produit obtenu avec un composé de formule

$R^1 - Y$

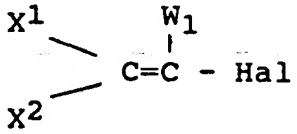
ou un sel d'un tel composé, ou
(b) avec un composé de formule

$R^1 - Y$

ou un sel d'un tel composé, puis la réaction du produit obtenu avec un composé de formule



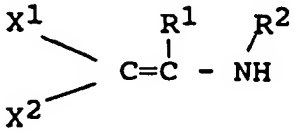
ou un sel d'un tel composé, ou
(4) la réaction d'un composé de formule



ou un sel d'un tel composé, avec un composé de formule

$Y - W^2$

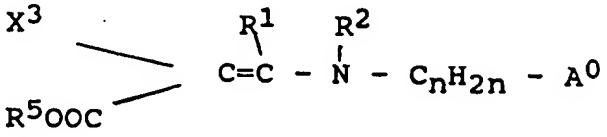
ou un sel d'un tel composé, ou
(5) la réaction d'un composé de formule



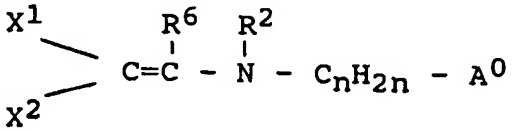
ou d'un sel d'un tel composé, avec un composé de formule

$A^0 - C_nH_{2n} - Hal$

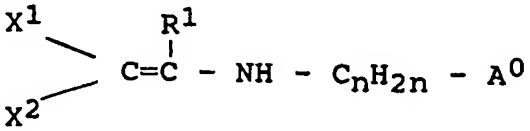
ou un sel d'un tel composé, ou
(6) le fait de soumettre un composé de formule



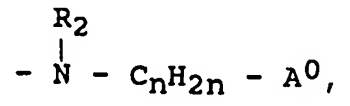
ou un sel d'un tel composé, à une réaction d'hydrolyse, puis à une réaction de décarboxylation, ou
(7) le fait de soumettre un composé de formule



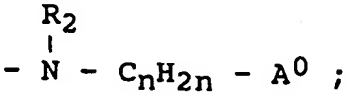
ou



ou un sel d'un tel composé, à une alkylation, une acylation, une alcoxycarbonylation, une sulfonylation ou une phosphorylation ;
dans les formules données ci-dessus, R^5 représente un groupe alkyle en C_{1-4} ou un groupe aralkyle ; quand W^1 représente



W^2 représente R^1, et quand W^1 représente R^1, W^2 représente



Y représente un atome d'hydrogène ou d'un métal alcalin ; R^3 représente un atome d'hydrogène ou un groupe alkyle, aryle, aralkyle, hétérocyclique, acyle, alcoxycarbonyle, aryloxycarbonyle, hétérocycle-oxycarbonyle, arylsulfonyle, alkylsulfonyle, dialcoxyphosphoryle, alcoxy, hydroxy, amino, dialkylamino, acylamino, alcoxycarbonylamino, alkylsulfonylamino, dialcoxyphosphorylamino, aralkyloxy ou alcoxycarbonylalkyle ; R^4 représente un atome d'hydrogène ou un groupe alkyle, cycloalkyle, alcényle, cycloalcényle ou alcynyle, lesquels groupes peuvent éventuellement être substitués, ou encore un groupe pyridyl-alkyle en C_{1-2} ou thiazolyl-alkyle en C_{1-2}, des fragments pyridyle et thiazolyle pouvant être éventuellement substitués par un atome d'halogène ; Hal représente un atome d'halogène ; X^3 représente un groupe électro-attracteur ; R^6 représente un groupe lié par un atome d'azote et contenant au moins un atome d'hydrogène ; et X^1, X^2, R^1, R^2, n et A^0 ont les définitions indiquées dans la revendication 1.

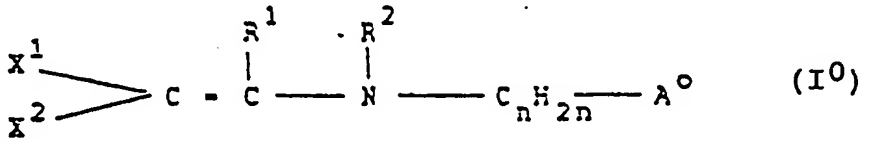
15. Procédé de lutte contre des insectes ou des acariens indésirables, qui comporte l'application, auxdits insectes ou acariens ou à leur habitat, d'une quantité efficace insecticide ou acaricide du composé de formule [I^0] défini dans l'une quelconque des revendications 1 à 12, ou d'un sel d'un tel composé.

16. Procédé conforme à la revendication 15, dans lequel le composé ou son sel est appliqué sous la forme d'une composition du composé ou du sel avec un ou des véhicules appropriés.

17. Procédé de lutte contre des insectes ou des acariens indésirables, qui comporte l'application d'une quantité efficace insecticide ou acaricide du composé de formule [I^0] défini dans la revendication 12.

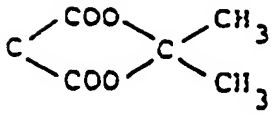
Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'une amine α-insaturée de formule :



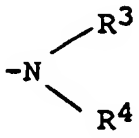
(I^0)

dans laquelle
l'un des X^1 et X^2 représente un groupe électro-attracteur et l'autre représente un atome d'hydrogène ou un groupe électro-attracteur, ledit groupe électro-attracteur étant un groupe cyano, nitro, (alcoxy en C_{1-4})-carbonyle, carboxy, (aryloxy en C_{6-10})-carbonyle, hétérocycle-oxycarbonyle, alkylsulfonyle en C_{1-4} qui peut être substitué par un atome d'halogène, aminosulfonyle, di-(alcoxy en C_{1-4})-phosphoryle, alcanoyle en C_{1-4} qui peut être substitué par un atome d'halogène, (alkyle en C_{1-4})-sulfonylthiocarbamoyle ou carbamoyle, ou encore un atome d'halogène, ou bien X^1 et X^2, conjointement avec l'atome de carbone auquel ils sont liés, forment un cycle de formule

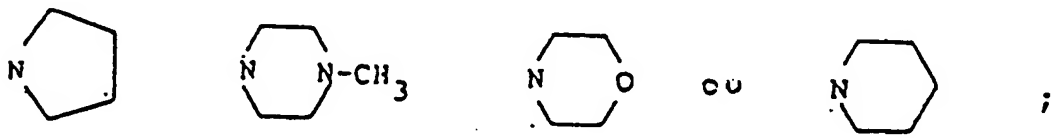


;

R^1 représente un groupe de formule

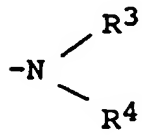


dans laquelle
R^3 représente un atome d'hydrogène ou un groupe alkyle en C_{1-20}, aryle en C_{6-10}, aralkyle en C_{7-9}, hétérocyclique, alcanoyle en C_{1-4}, (aryle en C_{6-10})-carbonyle, (alcoxy en C_{1-4})-carbonyle, (aryloxy en C_{6-10})-carbonyle, hétérocycleoxy-carbonyle, arylsulfonyle en C_{6-10}, alkylsulfonyle en C_{1-4}, di-(alcoxy en C_{1-4})-phosphoryle, alcoxy en C_{1-4}, hydroxy, amino, di-(alkyle en C_{1-4})-amino, alcanoylamino en C_{1-4}, (alcoxy en C_{1-4})-carbonylamino, alkylsulfonylamino en C_{1-4}, di-(alcoxy en C_{1-4})-phosphorylamino, aralkyloxy en C_{7-9} ou (alcoxy en C_{1-4})-carbonyl-(alkyle en C_{1-4}) ; et
R^4 représente un atome d'hydrogène ou un groupe alkyle en C_{1-20}, cycloalkyle en C_{3-6}, alcényle en C_{2-6}, cycloalcényle en C_{3-6} ou alcynyle en C_{2-6}, chacun des radicaux définis pour R^4, à l'exception de l'atome d'hydrogène, pouvant éventuellement porter de 1 à 3 substituants, choisis dans l'ensemble constitué par les atomes d'halogène et les groupes hydroxy, alcory en C_{1-4}, di-(alkyle en C_{1-4})-amino, alkylthio en C_{1-4}, alcanoylamino en C_{1-3}, alkylsulfonylamino en C_{1-4}, tri-(alkyle en C_{1-4})-silyle, pyridyle et thiazolyle, les groupes pyridyle et thiazolyle pouvant chacun être encore substitués par des atomes d'halogène ; ou bien
R^3 et R^4, conjointement avec l'atome d'azote adjacent, forment un groupe aminocyclique de formule :



;

R^2 représente (1) un atome d'hydrogène, (2) un groupe lié par un atome de carbone et choisi dans l'ensemble constitué par les groupes alcanoyle en C_{1-4}, alkyle en C_{1-20}, alcényle en C_{2-6}, cycloalkyle en C_{3-6}, aryle en C_{6-10}, aralkyle en C_{7-9}, 3-pyridyle et 4-pyridyle, ce groupe lié par un atome de carbone portant éventuellement de 1 à 3 substituants choisis dans l'ensemble constitué par les groupes alkylthio en C_{1-4}, alcoxy en C_{1-4}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, (alcoxy en C_{1-4})-carbonyle, alkylsulfonyle en C_{1-4} et alcanoyle en C_{1-4}, ainsi que par les atomes d'halogène, (3) un groupe lié par un atome d'oxygène et choisi dans l'ensemble constitué par les groupes alcoxy en C_{1-4}, cycloalcoxy en C_{3-6}, alcényloxy en C_{2-4}, cycloalcényloxy en C_{3-6}, éthynyloxy, aryloxy en C_{6-10}, thiényloxy et hydroxy, ce groupe lié par un atome d'oxygène pouvant éventuellement porter de 1 à 3 substituants choisis dans l'ensemble constitué par les atomes d'halogène et le groupe phényle, ou (4) un groupe lié par un atome d'azote, de formule :



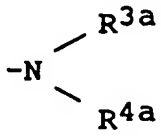
dans laquelle R^3 et R^4 ont les significations indiquées plus haut ;
n représente un nombre entier valant 0, 1 ou 2 ;
A^0 représente un hétérocycle ;
l'hétérocycle dudit groupe hétérocycle-carbonyle indiqué à propos de X_1 et X_2, ledit hétérocycle

indiqué à propos de R^3, l'hétérocycle dudit groupe hétérocycle-oxycarbonyle indiqué à propos de R^3, et ledit hétérocycle indiqué pour A^0 étant chacun un élément choisi dans l'ensemble constitué par les groupes thiényle, furyle, pyrrolyle, pyridyle, oxazolyle, thiazolyle, pyrazolyle, imidazolyle, isoxazolyle, isothiazolyle, oxadiazolyle, thiadiazolyle, triazolyle, tétrazolyle, N-oxydopyridyle, pyrimidinyle, N-oxydopyrimidinyle, pyridazinyle, pyrazinyle, N-oxydopyridazinyle, benzofuryle, benzothiazolyle, benzoxazolyle, triazinyle, oxotriazinyle, tétrazo[1,5-b]pyridazinyle, triazolo[4,5-b]pyridazinyle, oxoimidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle et phénoxazinyle, ledit hétérocycle pouvant éventuellement porter de 1 à 5 substituants choisis dans l'ensemble constitué de :

(I) alkyle en C_{1-4}
(II) cycloalkyle en C_{3-6}
(III) aryle en C_{6-10}
(IV) alcoxy en C_{1-4}
(V) cycloalkyloxy en C_{3-6}
(VI) aryloxy en C_{6-10}
(VII) aralcoxy en C_{7-12}
(VIII) alkylthio en C_{1-4}
(IX) cycloalkylthio en C_{3-6}
(X) arylthio en C_{6-10}
(XI) aralkylthio en C_{7-12}
(XII) mono-(alkyle en C_{1-4})-amino
(XIII) di-(alkyle en C_{1-4})-amino
(XIV) cycloalkylamino en C_{3-6}
(XV) arylamino en C_{6-10}
(XVI) aralkylamino en C_{7-12}
(XVII) halogéno
(XVIII) (alcoxy en C_{1-4})-carbonyle
(XIX) (aryloxy en C_{6-10})-carbonyle
(XX) (cycloalkyloxy en C_{3-6})-carbonyle
(XXI) (aralkyloxy en C_{7-12})-carbonyle
(XXII) alcanoyle en C_{1-5}
(XXIII) alcanoyloxy en C_{1-15}
(XXIV) carbamoyle, N-méthylcarbamoyle, N,N-diméthylcarbamoyle, N-éthylcarbamoyle, N,N-diéthylcarbamoyle, N-phénylcarbamoyle, pyrrolidinocarbamoyle, pipéridinocarbamoyle, pipérazinocarbamoyle, morpholinocarbamoyle ou N-benzylcarbamoyle
(XXV) N-méthylcarbamoyloxy, N,N-diméthylcarbamoyloxy, N-éthylcarbamoyloxy, N-benzylcarbamoyloxy, N,N-dibenzylcarbamoyloxy ou N-phénylcarbamoyloxy
(XXVI) alcanoylamino en C_{1-4}
(XXVII) (aryle en C_{6-10})-carbonylamino
(XXVIII) (alcoxy en C_{1-4})-carbonylamino
(XXIX) (aralcoxy en C_{7-12})-carbonyle
(XXX) méthanesulfonylamino, éthanesulfonylamino, butanesulfonylamino, benzènesulfonylamino, toluènesulfonylamino, naphtalènesulfonylamino, trifluorométhanesulfonylamino, 2-chloroéthanesulfonylamino ou 2,2,2-trifluoroéthanesulfonylamino
(XXXI) pyrrolidinyle, pyrrolyle, pyrazolyle, imidazolyle, furyle, thiényle, oxazolyle, isoxazolyle, isothiazolyle, thiazolyle, pipéridinyle, pyridyle, pipérazinyle, pyrimidinyle, pyranyle, tétrahydropyranyle, tétrahydrofuryle, indolyle, quinolyle, 1,3,4-oxadiazolyle, thiéno[2,3-d]pyridyle, 1,2,3-thiadiazolyle, 1,3,4-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1,3,4-triazolyle, tétrazolyle, 4,5-dihydro-1,3-dioxazolyle, tétrazolo[1,5-b]pyridazinyle, benzothiazolyle, benzoxazolyle, benzimidazolyle ou benzothiényle
(XXXII) les groupes hétérocycle-thio, hétérocycle-oxy, hétérocycle-amino ou hétérocycle-carbonylamino, qui dérivent du rattachement de l'un quelconque des groupes hétérocycliques (XXXI) définis ci-dessus à un atome S, O ou N ou à un groupe carbonylamino
(XXXIII) di-(alkyle en C_{1-4})-phosphinothioylamino
(XXXIV) méthoxyimino, éthoxyimino, 2-fluoroéthoxyimino, carboxyméthoxyimino, 1-carboxy-1-méthyl-éthoxyimino, 2,2,2-trichloroéthoxycarbonyl-méthoxyimino, 1-(2,2,2-trichloroéthorycarbonyl)-1-

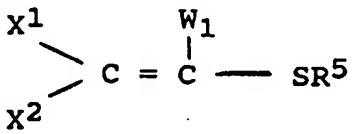
méthyl-éthoxyimino, (2-aminothiazol-4-yl)-méthoxyimino ou (1H-imidazol-4-yl)-méthoxyimino
(XXXV) alkylsulfonyloxy en C_{1-4}
(XXXVI) arylsulfonyloxy en C_{6-10}
(XXXVII) di-(aryle en C_{6-10})-phosphinothioylamino
(XXXVIII) thiocarbamoylthio, N-méthyl-thiocarbamoylthio, N,N-diméthyl-thiocarbamoylthio, N-éthyl-thiocarbamoylthio, N-benzyl-thiocarbamoylthio, N,N-dibenzyl-thiocarbamoylthio ou N-phényl-thiocarbamoylthio
(XXXIX) triméthylsilyloxy, t-butyl-diméthylsilyloxy, t-butyl-diphénylsilyloxy ou diméthyl-phénylsilyloxy,
(XL) triméthylsilyle, t-butyl-diméthylsilyle, t-butyldiphénylsilyle ou diméthyl-phénylsilyle
(XLI) alkylsulfinyle en C_{1-4}
(XLII) arylsulfinyle en C_{6-10}
(XLIII) alkylsulfonyle en C_{1-4}
(XLIV) arylsulfonyle en C_{6-10}
(XLV) (alcoxy en C_{1-4})-carbonyloxy
(XLVI) halogénoalkyle en C_{1-4}
(XLVII) halogénoalcoxy en C_{1-4}, halogénoalkylthio en C_{1-4}, halogénoalkylsulfinyle en C_{1-4} ou halogénoalkylsulfonyle en C_{1-4}
(XLVIII) cyano, nitro, hydroxy, carboxy, sulfo, phosphono
(XLIX) alcoxysulfonyle en C_{1-4}
(L) aryloxysulfonyle en C_{6-10}
(LI) aralcoxysulfonyle en C_{7-12}
(LII) di-(alcoxy en C_{1-4})-phosphoryle

sous réserve que, lorsque R^2 représente un atome d'hydrogène, R^1 représente un groupe de formule



dans laquelle R^{3a} représente un atome d'hydrogène ou un groupe alkyle en C_{1-4}, phénylalkyle en C_{7-9} ou alcanoyle en C_{1-4} et R^{4a} représente un atome d'hydrogène ou un groupe alkyle en C_{1-4}, (alcoxy en C_{1-4})-alkyle en C_{1-4}, [di-(alkyle en C_{1-4})-amino]-alkyle en C_{1-4}, tri-(alkyle en C_{1-4})-silyl-alkyle en C_{1-4}, alcényle en C_{2-4}, pyridylalkyle en C_{1-2} ou thiazolyl-alkyle en C_{1-2}, le fragment pyridyle ou thiazolyle pouvant éventuellement être substitué par un atome d'halogène, ou bien R^{3a} et R^{4a}, conjointement avec l'atome d'azote adjacent, forment un groupe pyrrolidino,
et A^0 représente un groupe pyridyle, pyrazinyle ou thiazolyle, dont chacun peut éventuellement être substitué par un atome d'halogène ou un groupe alkyle en C_{1-4}, alkylthio en C_{1-4} ou alcoxy en C_{1-4},
et sous réserve que, lorsque $X^1X^2C=$ représente $O_2N\text{-}CH=$, R^1 représente $-NR^3R^4$, R^3 représentant un atome d'hydrogène ou un groupe alkyle en C_{1-5} ou cycloalkyle en C_{3-6}, R^4 représentant un atome d'hydrogène ou un groupe alkyle en C_{1-5}, cycloalkyle en C_{3-6}, benzyle ou pyrimidinyl-méthyle, ou R^3 et R^4, conjointement avec l'atome d'azote adjacent, formant un groupe amino cyclique pyrrolidinyle ou pipérazinyle, et R^2 représente un atome d'hydrogène ou un groupe alkyle en C_{1-5} ou cycloalkyle en C_{3-6}, alors A^0 ne représente pas un groupe pyridyle substitué par un groupe halogénoalkyle en C_{1-4}, halogénoalcoxy en C_{1-4}, halogénoalkylthio en C_{1-4}, halogénoalkylsulfinyle en C_{1-4}, halogénoalkylsulfonyle en C_{1-4}, cyano, nitro ou hydroxy ; ou un sel d'un tel composé, ledit procédé comprenant :

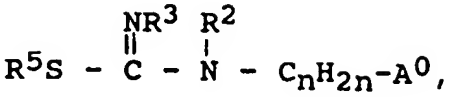
(1) la réaction d'un composé de formule

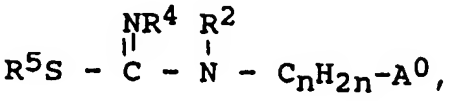


ou d'un sel d'un tel composé avec un composé de formule

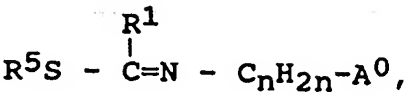
$Y - W^2$

ou un sel d'un tel composé, ou
(2) la réaction d'un composé de formule

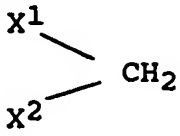




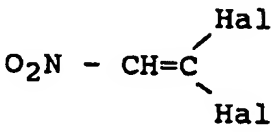
ou



ou d'un sel d'un tel composé, avec un composé de formule



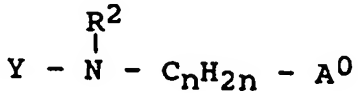
ou un sel d'un tel composé, ou
(3) la réaction d'un composé de formule



ou

$O_2N - CH_2C(Hal)_3$

(a) avec un composé de formule



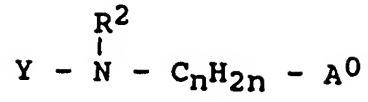
ou un sel d'un tel composé, puis la réaction du produit obtenu avec un composé de formule

$R^1 - Y$

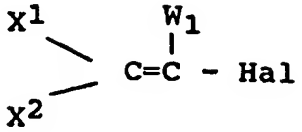
ou un sel d'un tel composé, ou
(b) avec un composé de formule

$R^1 - Y$

ou un sel d'un tel composé, puis la réaction du produit obtenu avec un composé de formule



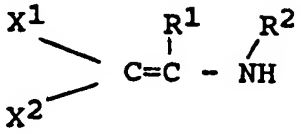
ou un sel d'un tel composé, ou
(4) la réaction d'un composé de formule



ou un sel d'un tel composé, avec un composé de formule

$Y - W^2$

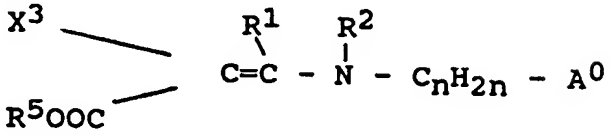
ou un sel d'un tel composé, ou
(5) la réaction d'un composé de formule



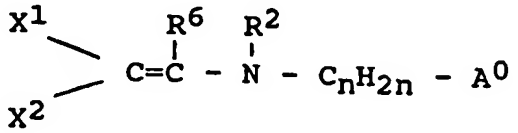
ou d'un sel d'un tel composé, avec un composé de formule

$A^0 - C_nH_{2n} - Hal$

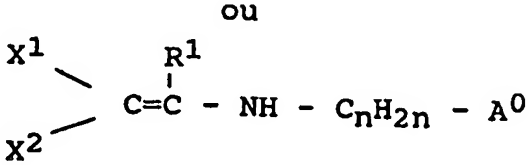
ou un sel d'un tel composé, ou
(6) le fait de soumettre un composé de formule



ou un sel d'un tel composé, à une réaction d'hydrolyse, puis à une réaction de décarboxylation, ou
(7) le fait de soumettre un composé de formule

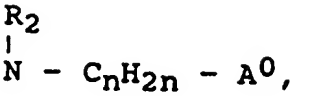


ou



ou un sel d'un tel composé, à une alkylation, une acylation, une alcoxycarbonylation, une sulfonylation ou une phosphorylation ;
dans les formules données ci-dessus, R^5 représente un groupe alkyle en C_{1-4} ou un groupe

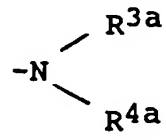
aralkyle ; quand W^1 représente



W^2 représente R^1, et quand W^1 représente R^1, W^2 représente

Y représente un atome d'hydrogène ou d'un métal alcalin ; R^3 représente un atome d'hydrogène ou un groupe alkyle, aryle, aralkyle, hétérocyclique, acyle, alcorycarbonyle, arylorycarbonyle, hétérocycle-oxycarbonyle, arylsulfonyle, alkylsulfonyle, dialcoxyphosphoryle, alcoxy, hydroxy, amino, dialkylamino, acylamino, alcoxycarbonylamino, alkylsulfonylamino, dialcoxyphosphorylamino, aralkyloxy ou alcoxycarbonylalkyle ; R^4 représente un atome d'hydrogène ou un groupe alkyle, cycloalkyle, alcényle, cycloalcényle ou alcynyle, lesquels groupes peuvent éventuellement être substitués, ou encore un groupe pyridyl-alkyle en C_{1-2} ou thiazolyl-alkyle en C_{1-2}, les fragments pyridyle et thiazolyle pouvant être éventuellement substitués par un atome d'halogène ; Hal représente un atome d'halogène ; X^3 représente un groupe électro-attracteur ; R^5 représente un groupe lié par un atome d'azote et contenant au moins un atome d'hydrogène ; et X^1, X^2, R^1, R^2, n et A^0 ont les définitions indiquées plus haut.

2. Procédé conforme à la revendication 1, dans lequel R^2 représente un atome d'hydrogène, R^1 représente un groupe de formule



dans laquelle R^{3a} et R^{4a} ont les définitions indiquées dans la revendication 1, et A^0 représente un hétérocycle choisi dans l'ensemble constitué par les groupes pyridyle, pyrazinyle et thiazolyle, cet hétérocycle que l'on vient de mentionner à propos de A^0 étant éventuellement substitué par un atome d'halogène ou un groupe alkyle en C_{1-4}, alkylthio en C_{1-4} ou alcoxy en C_{1-4}.

3. Procédé conforme à la revendication 1, dans lequel R^2 représente autre chose qu'un atome d'hydrogène.

4. Procédé conforme à la revendication 1, dans lequel

- X^1 représente un groupe nitro,
- X^2 représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-2})-carbonyle ou (alkyle en C_{1-2})-sulfonylthiocarbamoyle,
- R^1 représente un groupe amino, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, halogéno-(alkyle en C_{1-4})-amino, N-(alkyle en C_{1-4})-N-(alcanoyle en C_{1-2})-amino, N-(halogénoalkyle en C_{1-4})-N-(alcanoyle en C_{1-2})-amino ou (alcanoyle en C_{1-2})-amino,
- R^2 représente un atome d'hydrogène ou un groupe alcoxy en C_{1-2}, di-(alkyle en C_{1-2})-amino, alkyle en C_{1-4}, halogénoalkyle en C_{1-4} ou alcanoyle en C_{1-2},
- n vaut 0 ou 1,
- A^0 représente un groupe 2- ou 3-thiényle, 2- ou 3-furyle, 2- ou 3-pyrrolyle, 2-, 3- ou 4-pyridyle, 2-, 4- ou 5-oxazolyle, 2-, 4- ou 5-thiazolyle, 3-, 4- ou 5-pyrazolyle, 2-, 4- ou 5-imidazolyle, 3-, 4- ou 5-isoxazolyle, 3-, 4- ou 5-isothiazolyle, 3- ou 5-(1,2,4-oxadiazolyle), 1,3,4-oxadiazolyle, 3- ou 5-(1,2,4-thiadiazolyle), 1,3,4-thiadiazolyle, 4- ou 5-(1,2,3-thiadiazolyle), 1,2,5-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1H- ou 2H-tétrazolyle, N-oxydo-2-, 3- ou 4-pyridyle, 2-, 4-

ou 5-pyrimidinyle, N-oxydo-2-, 4- ou 5-pyrimidinyle, 3- ou 4-pyridazinyle, pyrazinyle, N-oxydo-3- ou 4-pyridazinyle, benzofuryle, benzothiazolyle, benzoxazolyle, triazinyle, oxotriazinyle, tétrazolo(1,5-b)pyridazinyle, triazolo(4,5-b)-pyridazinyle, oxoimidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinyle, quinolizinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle, chacun de ces groupes pouvant éventuellement être substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4}, halogénoalkyle en C_{1-4}, alcoxy en C_{1-4}, halogénoalcoxy en C_{1-4}, alkylthio en C_{1-4} ou halogénoalkylthio en C_{1-4},

ou d'un sel d'un tel composé.

5. Procédé conforme à la revendication 1, dans lequel

X^1 représente un groupe nitro,

X^2 représente un atome d'hydrogène ou un groupe (alkyle en C_{1-2})-sulfonylthio-carbamoyle,

R^1 représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino, halogéno-(alkyle en C_{1-2})-amino, N-(alkyle en C_{1-2})-N-(alcanoyle en C_{1-2})-amino, N-(halogénoalkyle en C_{1-2})-N-(alcanoyle en C_{1-2})-amino ou (alcanoyle en C_{1-2})-amino,

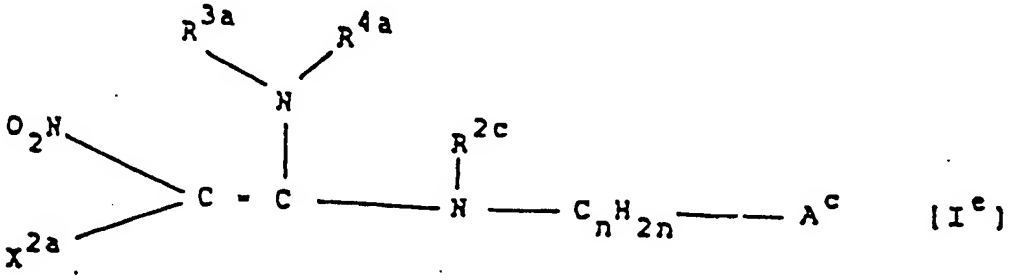
R^2 représente un atome d'hydrogène ou un groupe alcoxy en C_{1-2}, di-(alkyle en C_{1-2})-amino, alkyle en C_{1-4}, halogénoalkyle en C_{1-4} ou alcanoyle en C_{1-2},

n vaut 1, et

A^0 représente un groupe pyridyle, pyrazinyle ou thiazolyle, chacun de ces groupes pouvant éventuellement être substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4}, halogénoalkyle en C_{1-4}, alcoxy en C_{1-4}, halogénoalcoxy en C_{1-4}, alkylthio en C_{1-4} ou halogénoalkylthio en C_{1-4},

ou d'un sel d'un tel composé.

6. Procédé conforme à la revendication 1, pour la préparation d'un composé de formule



[I^e]

dans laquelle

X^{2a} représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-4})-carbonyle ou (alkyle en C_{1-4})-sulfonylthiocarbamoyle,

R^{2c} représente un atome d'hydrogène ou un groupe alcanoyle en C_{1-3}, alkyle en C_{1-4}, mono-(alcoxy en C_{1-4})-alkyle en C_{1-4}, di-(alcoxy en C_{1-4})-alkyle en C_{1-4}, aralkyle en C_{7-9}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino ou alcoxy en C_{1-4},

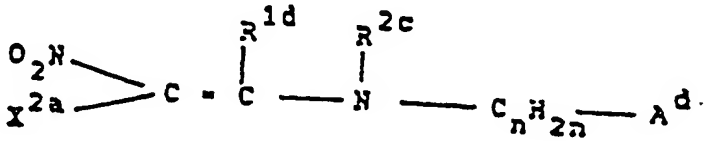
A^c représente un groupe 3-pyridyle, 4-pyridyle, pyrazinyle, 4-thiazolyle ou 5-thiazolyle, chacun de ceux-ci pouvant être éventuellement substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4} ou alcoxy en C_{1-4},

n vaut 1, et

R^{3a} et R^{4a} ont les définitions indiquées dans la revendication 1,

ou d'un sel d'un tel composé.

7. Composé conforme à la revendication 1, pour la préparation d'un composé de formule



[I^f]

dans laquelle

X^{2a} représente un atome d'hydrogène ou un groupe (alcoxy en C_{1-4})-carbonyle ou (alkyle en C_{1-4})-sulfonylthiocarbamoyle,

R^{1d} représente un groupe amino, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino, N-(alkyle en C_{1-4})-N-(alcanoyle en C_{1-3})-amino, aralkylamino en C_{7-9}, halogénothiazolyl-(alkyle en C_{1-2})-amino ou (alcoxy en C_{1-4})-(alkyle en C_{1-2})-amino,

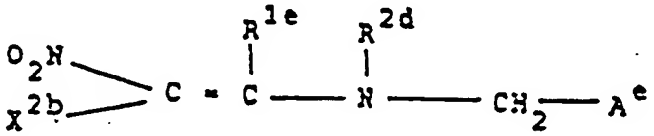
R^{2c} représente un atome d'hydrogène ou un groupe alcanoyle en C_{1-3}, alkyle en C_{1-4}, mono-(alcoxy en C_{1-4})-alkyle en C_{1-4}, di-(alcoxy en C_{1-4})-alkyle en C_{1-4}, aralkyle en C_{7-9}, mono-(alkyle en C_{1-4})-amino, di-(alkyle en C_{1-4})-amino ou alcoxy en C_{1-4},

n vaut 0, 1 ou 2, et

A^d représente un groupe 3-pyridyle, 4-pyridyle, pyrazinyle, ou 5-thiazolyle, chacun de ceux-ci pouvant être éventuellement substitué par des atomes d'halogène ou par des groupes alkyle en C_{1-4} ou alcoxy en C_{1-4},

ou d'un sel d'un tel composé.

8. Procédé conforme à la revendication 1, pour préparer un composé de formule



[I^g]

dans laquelle

X^{2b} représente un atome d'hydrogène ou un groupe (alkyle en C_{1-2})-sulfonylthiocarbamoyle,

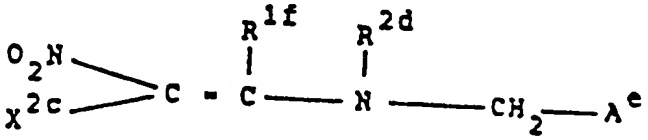
R^{1e} représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino ou N-(alkyle en C_{1-2})-N-formyl-amino,

R^{2d} représente un atome d'hydrogène ou un groupe alkyle en C_{1-2} ou alcanoyle en C_{1-3}, et

A^e représente un groupe de formule

où Hal représente un atome d'halogène,
ou un sel d'un tel composé.

9. Procédé conforme à la revendication 1, pour préparer un composé de formule



[I^h]

dans laquelle

X^{2c} représente un atome d'hydrogène ou un groupe méthylsulfonylthiocarbamoyle,

R^{1f} représente un groupe amino, méthylamino, diméthylamino ou N-méthyl-N-formylamino,

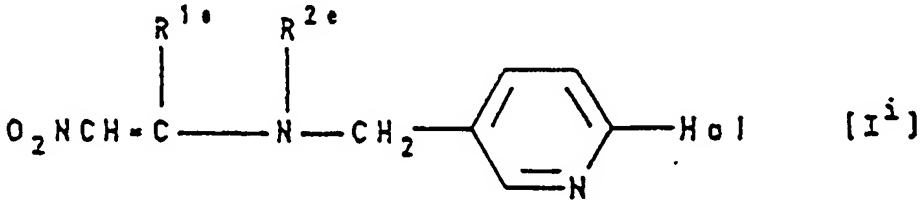
R^{2d} représente un atome d'hydrogène ou un groupe formyle ou alkyle en C_{1-2}, et

A^e représente un groupe de formule

où Hal représente un atome d'halogène,

ou un sel d'un tel composé.

10. Procédé conforme à la revendication 1, pour préparer un composé de formule



dans laquelle

R^{1e} représente un groupe amino, mono-(alkyle en C_{1-2})-amino, di-(alkyle en C_{1-2})-amino ou N-(alkyle en C_{1-2})-N-formyl-amino,

R^{2e} représente un groupe alkyle en C_{1-2} ou formyle, et

Hal représente un atome d'halogène,

ou un sel d'un tel composé.

11. Procédé conforme à la revendication 1, dans lequel l'hétérocycle est choisi dans l'ensemble suivant et éventuellement substitué comme indiqué dans la revendication 1, ledit ensemble étant constitué par les groupes 2- ou 3-thiényle, 2- ou 3-furyle, 2- ou 3-pyrrolyle, 2-, 4- ou 5- oxazolyle, 2-, 4- ou 5-thiazolyle, 3-, 4- ou 5-pyrazolyle, 2-, 4- ou 5-imidazolyle, 3-, 4- ou 5-isoxazolyle, 3-, 4- ou 5-isothiazolyle, 3- ou 5-(1,2,4-oxadiazolyle), 1,3,4-oxadiazolyle, 3- ou 5-(1,2,4-thiadiazolyle), 1,3,4-thiadiazolyle, 4- ou 5-(1,2,3-thiadiazolyle), 1,2,5-thiadiazolyle, 1,2,3-triazolyle, 1,2,4-triazolyle, 1H- ou 2H-tétrazolyle, N-oxydo-2-, 3- ou 4-pyridyle, 2-, 4- ou 5-pyrimidinyle, N-oxydo-2-, 4- ou 5-pyrimidinyle, 3- ou 4-pyridazinyle, pyrazinyle, N-oxydo-3-ou 4-pyridazinyle, benzofuryle, benzo-thiazolyle, benzoxazolyle, triazinyle, oxo-triazinyle, tétrazolo(1,5-b)pyridazinyle, triazolo(4,5-b)pyridazinyle, oxo-imidazinyle, dioxotriazinyle, pyrrolidinyle, pipéridinyle, pyranyle, thiopyranyle, 1,4-oxazinyle, morpholinyle, 1,4-thiazinyle, 1,3-thiazinyle, pipérazinyle, benzimidazolyle, quinolyle, isoquinolyle, cinnolinyle, phtalazinyle, quinazolinyle, quinoxalinyle, indolizinyle, quinolisinyle, 1,8-naphtyridinyle, purinyle, ptéridinyle, dibenzofuranyle, carbazolyle, acridinyle, phénanthridinyle, phénazinyle, phénothiazinyle ou phénoxazinyle.

12. Procédé conforme à la revendication 1, pour préparer un composé choisi parmi le 1-[N-(6-chloro-3-pyridylméthyl)-N-méthyl]amino-1-méthylamino-2-nitroéthylène, le 1-(6-chloro-3-pyridyl-méthyl)amino-1-diméthylamino-2-nitroéthylène, et le 1-[N-(6-chloro-3-pyridylméthyl)-N-éthyl]amino-1-méthylamino-2-nitroéthylène.

13. Procédé de préparation d'une composition insecticide/acaricide, qui comprend le fait de mélanger une quantité efficace insecticide/acaricide d'au moins l'une des amines α-insaturées préparées selon l'une quelconque des revendications 1 à 12, ou d'un sel d'une telle amine, avec un ou des véhicules appropriés.

14. Procédé de lutte contre des insectes ou des acariens indésirables, qui comporte l'application, auxdits insectes ou acariens ou à leur habitat, d'une quantité efficace insecticide ou acaricide du composé de formule [I^0] préparé selon l'une quelconque des revendications 1 à 12, ou d'un sel d'un tel composé.

15. Procédé conforme à la revendication 14, dans lequel le composé ou son sel est appliqué sous la forme d'une composition du composé ou du sel avec un ou des véhicules appropriés.